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Pulp and paper

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PULP AND PAPER

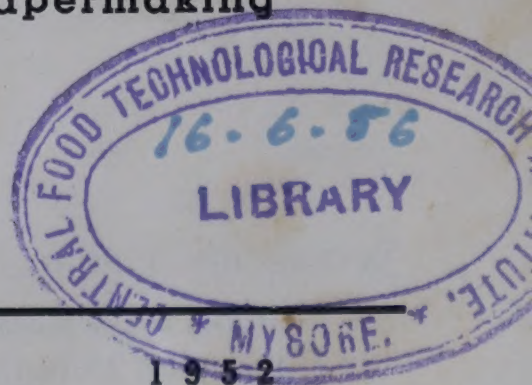
Chemistry and Chemical Technology

IN TWO VOLUMES

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JAMES P. CASEY, *Director of Technical Service*
A. E. Staley Manufacturing Company, Decatur, Illinois
Formerly Associate Professor of Pulp and Paper Manufacture
State University of New York, College of Forestry, Syracuse,
New York

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PREFACE

It is possible to divide the principles of papermaking into those which are chemical and those which belong in the field of engineering. This book is concerned primarily with the subjects relating to chemistry.

Papermaking is essentially a chemical process, although the remarkable engineering achievements of the industry have often obscured this fact. The maze of intricate mechanical operations necessary in the modern paper mill makes it difficult, for the casual observer at least, to realize that the final object of all this effort is the modification and rearrangement of the papermaking fibers. It should be realized, however, that these intricate machines are merely tools for carrying out the various chemical operations necessary to the formation of a sheet of paper. This method of thought will become more widespread since, as seems likely, the important developments of the future will be in the field of applied chemistry.

Unlike many of our modern chemical industries, the paper industry had its origin in antiquity. The knowledge and methods of papermaking were handed down to a select few in an attempt to keep them as secret as possible, and this practice was carried into modern times. As a result, our knowledge has increased slowly, and many of the processes used today show but little change over those used by the medieval papermaker. In the last thirty years, however, a marked change has taken place. Secrecy has given way to cooperation in the sharing of ideas. The change has been due to the entrance of scientifically trained personnel from such well-known institutions as the College of Forestry of the State University of New York, the Institute of Paper Chemistry, the University of Maine, Massachusetts Institute of Technology, and many others. Another important factor has been the growth of the Technical Association of the Pulp and Paper Industry, which has promoted research and interchange of ideas through its various publications and other activities. Much has been done to make available technical facts, data, and standards that have been highly useful to the paper mill chemist. There are several good books available on the technological aspects of making and using paper, and much has been published in current literature.

However, in the author's opinion, there has been too little emphasis placed on the fundamental chemistry of paper, its manufacture, and use. This book is an attempt to present such fundamental information on paper. It approaches the study of the papermaking raw materials and processes from the standpoint of the colloid and physical chemist. Although there

is a general awakening to the fact that all forces of science are the same, it is still convenient and useful to study the sciences separately, and further to divide the science of chemistry into several branches. As long as this division is desirable, it is logical to study papermaking with the special concepts and tools of colloid and physical chemistry. Colloid chemistry is that branch of chemistry that deals with systems in which surface is the most important factor, and the process of papermaking is therefore a colloidal phenomenon, involving as it does the control and interaction of surfaces in the beating and felting of fibers. Dyeing, sizing, filling and coating are colloid chemical processes utilizing materials that are almost without exception classified as colloids. It is the concepts of colloid chemistry which are of the greatest importance to an understanding of the papermaking processes and which, at the same time, are least understood by the average paper mill chemist.

An attempt has been made to present the material in fundamental terms, and yet at the same time to bridge the gap between strict theory on one hand and extreme empiricism on the other. This middle ground is the fertile field for the growth of new ideas which may eventually become worth while, and an effort has been made to keep this book within that scope. The new concepts of cellulose and lignin, the host of new sizing agents, coatings, adhesives, fillers, etc., warrant considerable study by paper mill chemists. A thoroughgoing understanding of the chemistry of these new materials, as well as the older, more familiar ones, will open up new possibilities in the paper field. It is with this idea in mind that the book has been written.

The author believes that the day is past when it is necessary to write a book on papermaking which must, of necessity, be understandable to the paper mill machine tender and superintendent. The chemist has taken his rightful place in the paper mill. He is specially trained for, and should have the time to devote his energies to, process development, improvement, and control, whereas the superintendent is often not equipped by training, and is too busy with current production, to do so. That the chemists' efforts have been fruitful is attested to by the recent developments of the paper industry, such as the broadening in the number of wood species used, improved pulping and bleaching processes, the development of wet-strength papers, waterproof papers, paper-base plastics, coated papers, and many others, all of which have been the results of the cooperative efforts of the chemists of the industry. This book has been written for the chemist who has more than a casual interest in the paper industry. It is hoped that it will be of value both to advanced students (that is, seniors and graduate students) and to chemists who are already working in the paper and allied industries. It has been written for use as a text book and a reference book.

In conclusion, the author wishes to point out that, although he wrote the original manuscript himself, the final work is the result of many helpful

comments by a number of experts in the paper industry. In attempting to write the book by himself, the author realized the hazards of one man's trying to cover such an extensive industry. On the other hand, there were the disadvantages of group writing to be considered, particularly in the lack of continuity which usually results. An attempt was made to find at least one qualified expert to review each section of the book. To all these men, the author owes a debt of gratitude. It is impossible to give full credit, but the names of some of those who aided in the writing are mentioned below.

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J.P.C.

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CELLULOSE AND HEMICELLULOSE

The basic raw material for papermaking is cellulose which, fortunately for the papermaker, occurs in the form of fibers in a wide variety of growing plants. Cellulose is a carbohydrate which comprises the major portion of the wall tissue of most plant cells. Cellulose exists as bast fibers, tracheids, or wood fibers, and in certain plants, notably cotton, as seed hair fibers. Seed hair fibers are quite pure cellulose, but the cellulose in woody tissue is associated with lignin, hemicelluloses, and other substances.

Wood is the principal source of commercial cellulose, but cellulose is also obtained from cotton, straws, and other non-woody plants. The approximate cellulose content of a few representative materials used for papermaking is given below:

Raw material	Per cent Cellulose
Seed hairs (e.g., cotton)	90
Bast fibers (e.g., flax)	80
Wood (e.g., spruce)	60
Stems (e.g., straw)	30

Cellulose derived from different sources differs in chemical and physical properties, as well as in structural cell type. The latter is an important consideration from a papermaking standpoint, since it is the fibrous structure of the cellulose which makes it useful as a papermaking raw material.

Types of Cellulose

As pointed out above, the cellulose in wood is associated with a variety of different "impurities" which consist of other carbohydrates referred to as hemicelluloses, as well as non-carbohydrate materials such as lignin, mineral matter, and resins. Separation of the cellulose from these "impurities" is necessary in the manufacture of most grades of commercial pulp, since too high a percentage of these impurities lowers the quality of the pulp.

Pulping and bleaching processes involving both physical and chemical treatment of the raw material are used commercially for the separation of cellulose. In the laboratory, the chemist uses somewhat different tech-

niques for the isolation of cellulose from plant raw material, since he is interested in obtaining the cellulose in as close to the native state as possible. However, it is virtually impossible to isolate cellulose from the other constituents of wood without some degradation, no matter how selective the technique, and hence it is advisable in referring to the various forms of isolated cellulose to use exact terminology descriptive of the raw material and method of isolation, for example, straw holocellulose and bleached sulfite pulp from spruce.

Some of the various descriptive terms used in reference to cellulose are described below. In all references to cellulose, it should be kept in mind that the physical and chemical properties of pure cellulose are quite different from the properties of the impure forms of cellulose used by the papermaker, since impurities in the latter often exert a profound influence on the properties.

Alpha Cellulose

Alpha cellulose is a term used to define the "true" cellulose content of plant material in terms of alkali solubility. Alpha cellulose is not an actual chemical type but is that portion of the plant cellulose which is insoluble in 17.5% sodium hydroxide at 20° C. under certain specified conditions. Beta cellulose is that fraction of the cellulose which is soluble in 17.5% sodium hydroxide, but which precipitates out of solution when acidified. Gamma cellulose is that fraction which is soluble in alkali of the above strength and which is not precipitated on neutralization. The beta and gamma cellulose fractions often include a considerable amount of hemicelluloses and degraded cellulose.

Alpha cellulose is usually determined by a gravimetric method whereby the fraction insoluble in 17.5% sodium hydroxide is filtered and weighed.¹ Beta and gamma celluloses can also be determined by gravimetric methods, but they are much more difficult to handle because of their gelatinous nature. The tests are empirical and must be carried out under carefully controlled conditions. The sample must be properly disintegrated before treatment,² and the weighing of the dried residue must be done very carefully, using tightly covered bottles, since dried alpha cellulose is very hygroscopic.³ On the other hand, the concentration of alkali, ratio of alkali to pulp, and time of treatment are not as critical as might be expected, and these variables can be varied within reasonable limits without affecting the results.^{4, 5}

¹ See TAPPI Standards

² B. L. Browning, *Paper Trade J.* 124, No. 15: 158-160 (Apr. 10, 1947)

³ A. S. O'Brien, L. K. Reitz and R. C. Bloom, *Paper Trade J.* 127, No. 6: 340-343 (Aug 5, 1948)

⁴ C. K. Bump, *Ind. Eng. Chem., Anal. Ed.* 6: 223 (1934)

⁵ G. J. Ritter, *Ind. Eng. Chem., Anal. Ed.* 1: 52 (1929)

Alpha cellulose is not a definite homogeneous material, but rather is an empirically defined fraction of the cellulose containing cellulose molecules of different molecular weights. The alpha cellulose fraction of unbleached wood pulps contains a high percentage of the lignin that must be compensated for by making a lignin determination on the residue, or by delignifying the sample with sodium chlorite before making the alpha cellulose determination.⁶ Alpha pulps are pulps which are high in alpha cellulose content. They are discussed in Chapter V, "Bleaching."

Holocellulose

Holocellulose is a term used to refer to the total carbohydrate fraction of plant raw material which is left after the lignin is removed. Some of the methods used for the isolation of holocellulose from wood are: (1) treatment of wood meal with chlorine, followed by extraction with alcoholic monoethanolamine; (2) treatment of extractive-free wood with chlorine, followed by alkali extraction; (3) treatment of the wood with acidified sodium chlorite.

In preparing holocellulose from wood by the chlorine method,⁷ the wood is first ground to a size between 40 and 60 mesh and then is extracted with 95% alcohol, with alcohol-benzene, and finally with hot water. After extraction, the sample is chlorinated for three minutes by passing chlorine gas through a funnel inverted over the sample on a suction flask. After rechlorinating for two minutes, the sample is washed with alcohol, alcohol-monoethanolamine, alcohol, and twice with cold water. The sample is then rechlorinated, extracted, and washed until there is no color upon chlorination and washing with alcohol-monoethanolamine. The sample is then washed with alcohol until neutral and finally with ether.

Holocellulose contains nearly 100% of the carbohydrates in the original raw material, although there is some loss of hemicelluloses in the case of the softwoods.⁸ In general, however, the holocellulose plus the lignin accounts for 100% of the weight of extractive-free wood. Small amounts of foreign substances may be present in holocellulose (e.g., polygalacturonides). The yield of holocellulose varies from about 65 to 73% for softwoods to about 70 to 82% for hardwoods. White spruce contains about 73% and quaking aspen about 82%.⁹ Holocellulose contains about 10 to 14% more of the alpha cellulose than most commercial papermaking pulps.

⁶ P. F. Cundy and M. M. Beck, *Paper Trade J.* 124, No. 18: 194-195 (May 1, 1947)

⁷ See TAPPI Standards

⁸ E. C. Jahn and C. V. Holmberg, *Paper Trade J.* 109, No. 13: 164-169 (Sept. 28, 1939)

⁹ H. J. Perry, *Paper Ind.* 31, No. 2: 210-213 (May, 1949)

Cross and Bevan Cellulose

Another method of isolating cellulose is the Cross and Bevan method developed in 1880 and later modified. Briefly, this method consists of subjecting the raw material while in a moist state to chlorine gas for three to four minutes, after which the sample is washed with water, sulfur dioxide solution, and a solution of about 2% sodium sulfite to remove all the lignin and a specific fraction of the hemicellulose.¹⁰ Several chlorinations, followed by treatment with sodium sulfite, may be necessary in order to remove the last traces of lignin. The various steps should be repeated until the fibers show only a faint tinge of pink upon addition of sodium sulfite. Prolonged chlorination should be avoided in order to prevent degradation of the cellulose.

Cross and Bevan cellulose is slightly more degraded than holocellulose, but it is less severely degraded than the cellulose in commercial pulps. It consists of nearly all the "true" cellulose in the original wood, but only a part of the hemicelluloses (mostly the celluloses, but not the polyuronides). Like the original cellulose in wood, Cross and Bevan cellulose is not a homogeneous substance, but rather is a mixture of the "true" cellulose with carbohydrates of lower molecular weight. Cross and Bevan cellulose contains about 5% less alpha cellulose than holocellulose. The lignin content of Cross and Bevan cellulose usually varies from 0.1 to 0.3%.

Chemical Properties of Cellulose

The chemical properties of cellulose are, for some purposes, of more importance than the physical form of the cellulose. The chemical properties are of obvious importance in the manufacture of cellulose derivatives, but their importance in papermaking, which is almost as great, is sometimes overlooked.

The chemical properties of cellulose cannot be regarded as fixed, since cellulose undergoes appreciable chemical change upon aging, as evidenced by the deterioration which occurs during the storage of pulp and the aging of paper. Samples taken for test should be protected from the degrading influences of heat, light, air, acidity, and similar influences.

Molecular Structure

An insight into the molecular structure of cellulose was first obtained when it was shown that cellulose can be quantitatively hydrolyzed to glucose, indicating that the cellulose molecule is composed of a series of glucose units. Later, it was shown that each glucose unit in the cellulose molecule contains three free hydroxyl groups, composed of two secondary alcohol groups and one primary alcohol group, which are arranged in positions 2,

¹⁰ See TAPPI Standards

3, and 6, respectively, on the glucose unit. Hence, the glucose units are linked together by 1,4-glucosidic oxygen bonds which, since they can be hydrolyzed by emulsin, must be in the beta form. The cellulose molecule thus consists of a long, straight chain of glucose anhydride units arranged in cellobiose pairs, as represented by the formula in Figure I-1.

The alcohol groups in the cellulose molecule undergo typical alcohol reactions, i.e., alcoholate formation, ester formation, oxidation, etc. These groups are responsible for the hydrophilic nature of cellulose and they, together with the fact that the individual glucose units are bound together by acid-sensitive acetal linkages, explain many of the reactions which cellulose undergoes.

In addition to alcohol groups, wood cellulose ordinarily contains a number of carboxyl groups. These groups are few in number unless the cellulose has been seriously degraded, but they are present in sufficient number that cellulose acts as a weak monobasic acid having an ionization constant of approximately 2.0×10^{-14} .¹¹ The carboxyl groups occur at a

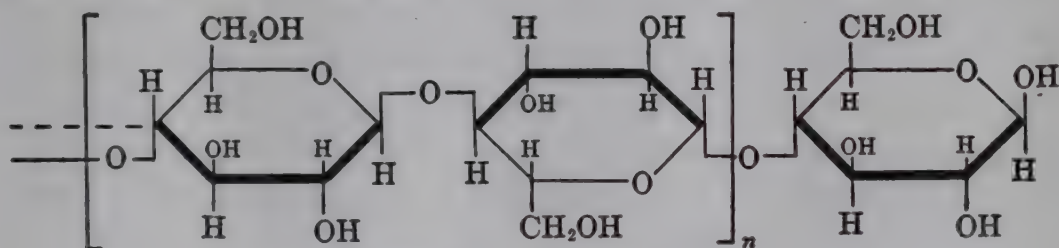


Fig. I-1. Cellulose.

frequency of about one for every hundred or more glucose units. They are located mainly in the number 6 position, although they may also be found in the number 2 and 3 positions.

Chain Length and Molecular Weight

Considerable effort has been expended in an attempt to determine the chain length and molecular weight of cellulose as it exists in the plant. Such information would be of great value in assessing the degradation that occurs during the commercial isolation of cellulose, but so far, no completely reliable data have been obtained, principally because of the uncertainty regarding the amount of degradation involved in all analytical procedures used for the removal of cellulose from the plant. Information on the chain length and molecular weight of the cellulose in commercial pulps is of practical value because of the relationship which exists between the average chain length and the physical properties of cellulose fibers. In general, the greater the chain length of the constituent cellulose molecules, the stronger the fiber and the more resistant it is to the degrading effects of heat and chemicals and biological attack.

¹¹ S. M. Neale, *J. Textile Inst.* 20: T373 (1929)

Part of the difficulty in analyzing wood cellulose is derived from the fact that wood cellulose is highly polymolecular in that it contains molecules of widely varying chain length. This polymolecularity of cellulose makes it necessary to report results of chain length measurements on the basis of the average. Part of the short-chain material present in isolated commercial cellulose may very likely be present in the original plant, but a considerable portion of the short-chain material in commercial pulps is probably the result of degradation occurring during the pulping and bleaching processes. Cotton cellulose is less polymolecular than wood cellulose, but it, too, contains molecules of different length, although it differs from wood cellulose in the absence of short-chain material up to a degree of polymerization (D.P.) of about 1,400.¹²

Because of its polymolecular nature, it is inadequate to judge cellulose by its average D.P. alone, without taking into account the chain-length distribution. Two commercial pulps may have very nearly the same average D.P. and yet differ widely in chain-length distribution, and, consequently, in their physical properties. Heuser and Jörgensen¹³ have pointed out that a certain type of sulfite pulp (Mitscherlich pulp) has considerable portions of very long and very short chain materials, and that this explains the unusual properties which this pulp possesses. However, average D.P. is a relatively easy measurement to make and is frequently used as an indication of the quality of cellulose.

Of the methods for determining the average chain length and molecular weight of cellulose, the most important are by x-ray diffraction, viscosity measurements, ultracentrifuge methods, and end-group determinations. These methods generally give results in close agreement for simple polymers, but unfortunately, in the case of cellulose there has been considerable discrepancy in the results obtained with these various methods. Part of the discrepancy has been due to inherent variability between the tests, since widely different values have been obtained on the same sample of cellulose when different methods were used. Other cases of serious disagreement can be attributed to the use of samples containing badly degraded cellulose. In general, viscometric and ultracentrifuge methods^{13a} give higher values than those obtained by x-ray analysis¹⁴ and end-group determinations.¹⁵

The average D.P. of undegraded cotton cellulose is very high, about 3,000 to 5,000. The D.P. of wood cellulose is also very high (2,500 or higher), but it is easily reduced by chemical treatment, such as pulping.

¹² E. Heuser, *Tappi* 33, No. 3: 118-124 (Mar., 1950)

¹³ E. Heuser and L. Jörgensen, *Tappi* 34, No. 2: 57-67 (Feb., 1951)

^{13a} A. J. Stamm, *J. Am. Chem. Soc.* 52: 3047-3067 (Aug., 1930)

¹⁴ S. H. Clarke, *Paper-Maker* 110, No. 6: TS53-54 (Dec., 1945)

¹⁵ H. N. Haworth and H. Machemer, *J. Chem. Soc.* 2270-2277 (Aug. 3, 1932)

Kraemer¹⁶ reports a D.P. of over 3,500 for native cotton cellulose compared with 600 to 1,000 for commercial wood pulps. By multiplying the D.P. by 162, the molecular weight of a single glucose unit, the average molecular weight of cellulose can be obtained. Representative values for molecular weight reported by Kraemer are over 570,000 for native cellulose, 150,000 to 500,000 for purified cotton linters, and 90,000 to 150,000 for commercial wood pulp. More recent work indicates still higher D.P. values covering a range of 1,500 to 3,500 for commercial materials and 6,000 to 8,000 for native materials.¹⁷ Non-cellulosic carbohydrates, of course, have a much lower D.P. than cellulose. Some of the values reported in the literature are 140 to 200 for beta cellulose,^{18, 19} 10 to 140 for gamma cellulose,²⁰⁻²² 150 to 160 for undegraded xylan and mannan,^{23, 24} and 70 for hemicellulose.²⁵

Hydrocellulose

Cellulose is degraded by acids to a product of lower molecular weight which is known as hydrocellulose. Hydrocellulose is produced whenever cellulose is left in acid media for long periods of time, particularly if the temperature is high. Nitric, sulfuric, and hydrochloric acids are particularly active, whereas phosphoric acid is less so. Oxalic acid is quite active, but other organic acids are not.

The initial attack of dilute mineral acids is quick and drastic, although the action tends to become more or less stabilized at a point where the cellulose chain contains about 320 glucose units.²⁷ The effect of concentrated acids is somewhat different from that of dilute acids; for example, strong sulfuric acid (78% solution) gelatinizes cellulose; strong nitric acid results in ester formation. Cellulose dissolved in strong phosphoric acid at low temperatures is said to undergo very little hydrolysis.²⁸

If the action of acids is carried far enough, cellulose fibers are converted into a friable white or cream-colored powder. Under extremely drastic conditions, the end products are simple sugars. Ordinarily, however, hydrolysis never proceeds to this extent. Cellulose fibers subjected to relatively mild acid conditions retain their fibrous structure, although

¹⁶ E. O. Kraemer, *Ind. Eng. Chem.* 30, No. 10: 1200-1203 (Oct., 1938)

¹⁷ H. F. Mark, *Tappi* 32, No. 3: 108-109 (Mar., 1949)

¹⁸ R. Vincent, *Paper Trade J.* 122, No. 4: 31-35 (Jan. 24, 1946)

¹⁹ H. Staudinger and I. Jurisch, *Kunstseide u. Zellwolle* 21: 6-9 (1939)

²⁰ E. O. Kraemer, *Ind. Eng. Chem.* 30, No. 10: 1200-1203 (Oct., 1938)

²¹ R. Vincent, *Paper Trade J.* 122, No. 4: 31-35 (Jan. 24, 1946)

²² H. Staudinger and I. Jurisch, *Kunstseide u. Zellwolle* 21: 6-9 (1939)

²³ R. Vincent, *Paper Trade J.* 122, No. 4: 31-35 (Jan. 24, 1946)

²⁴ H. Staudinger and I. Jurisch, *Kunstseide u. Zellwolle* 21: 6-9 (1939)

²⁵ R. L. Mitchell, *Ind. Eng. Chem.* 38, No. 8: 843-850 (Aug., 1946)

²⁷ E. Pasco, Textile Research Institute, 17th Annual Meeting (Nov. 8, 1946)

²⁸ TAPPI Monograph No. 6: "Nature of the Chemical Components of Wood." P. 34. Tech. Assoc. of the Pulp and Paper Industry, New York, N. Y. (1948)

the solubility in water and alkali is increased and the tensile strength of the fibers is reduced.

In several places in the papermaking process prevailing conditions are sufficiently acid to result in degradation of the fibers. Sulfite pulping is the most notable example. The loss of strength of paper upon aging, particularly when the pH of the paper is low, is another example of acid degradation.

Oxycellulose

Cellulose is highly susceptible to oxidizing agents. These cause cellulose to break down into a product of lower molecular weight, called oxycellulose. Oxycellulose may vary from practically unchanged fibers to a friable powder, depending upon the severity of the oxidation. A wide variety of products may be produced, depending upon the oxidizing agent and the conditions of oxidation, but recent evidence points to two basic types of oxycellulose—that produced in acid medium and that produced in neutral and alkaline medium. Oxycellulose produced under acid conditions resembles hydrocellulose in its properties, whereas oxycellulose produced under neutral or alkaline conditions is quite different.

The action of hypochlorite on cellulose under neutral or alkaline conditions produces an oxycellulose containing a relatively high percentage of carboxyl groups. On the other hand, periodate oxycellulose contains a large number of carbonyl groups.²⁹ These groups result from the oxidation of a part of the alcoholic hydroxyl groups in the cellulose molecules. A satisfactory estimation of the number of carboxyl groups in oxycellulose can be obtained by the methylene blue test, in which methylene blue (a basic dye) is held by salt formation at definite points on the cellulose molecule corresponding to the presence of carboxyl groups.³⁰ Another test^{31, 32} involves titration of a suspension of the oxycellulose in water with the silver salt of a very weak acid (e.g., silver ortho-nitrophenolate). Another method is by measurement of displacement of acetic acid from aqueous calcium acetate.³³

Cellulose is subject to possible oxidation at several points in the papermaking process. Bleaching of pulp with chlorine and hypochlorite are processes in which oxidative degradation is most likely to occur; for ex-

²⁹ M. O. Schur and R. M. Levy, *Paper Trade J.* 124, No. 20: 221–224 (May 15, 1947)

³⁰ D. Krüger, *Kleppzig's Textil-A.* 44: 647–650 (1941) through *C. A.* 36: 5641

³¹ A. M. Sookne and M. Harris, *Am. Dyestuff Rept.* 30, No. 5: 107–108 (Mar. 3, 1941)

³² B. Meesook and C. B. Purves, *Paper Trade J.* 123, No. 18: 223–230 (Oct. 31, 1946)

³³ E. C. Yackel and W. O. Kenyon, *J. Am. Chem. Soc.* 64, No. 1: 121–127 (Jan. 1942)

ample, Staudinger and Jurisch³⁴ found that cellulose was reduced in D.P. from 1,200 to about 205 after exposure to chlorine water for five hours at 20° C. Another place where oxidation is likely to occur is in the alkaline purification of pulp. Some oxidation occurs when paper is heated at high temperatures in accelerated aging tests. In the viscose process for making rayon, controlled oxidation is utilized as a means of reducing the molecular weight of the cellulose to the desired value.

Heat-Degraded Cellulose

Heat has, in some respects, a more degrading influence on cellulose than mild acids or mild oxidizing agents.³⁵ Cellulose fibers which have been dried at excessively high temperatures, or overdried, lose some of their valuable papermaking qualities, which cannot be successfully recovered by putting moisture back into the fibers. The effect of heat is principally due to dehydration, which, if carried far enough, results in an appreciable loss in hygroscopicity and swelling ability of the fibers.³⁶ The loss in hygroscopicity and swelling ability on heating can be explained (1) by increased hydrogen bonding between adjacent cellulose molecules or (2) by the formation of chemical linkages between adjacent cellulose molecules as, for example, by the formation of ether linkages.³⁷ The loss in swelling ability resulting from prolonged heating of wood pulp fibers at temperatures of about 100° C. may be as much as 50%.³⁸

Cellulose fibers heated at elevated temperatures have greatly reduced tensile strength and are very fragile.³⁹ If heated at temperatures over 200° C. for long periods of time, a complete loss in fiber structure results. Even in the presence of moisture, cellulose fibers lose considerable strength if heated at 150° C. or higher in the presence of air.

Viscosity of Cellulose Solutions

A number of tests are used to measure the properties of cellulose, some of which have already been mentioned, and one of the most important of these is the viscosity of cellulose in solution. This test is one of the standard tests used for measuring the average chain length of cellulose molecules. On the basis of the molecular chain theory for the structure of cellulose, a low viscosity reading is regarded as an indication of low average chain length. In the range of high viscosities, the viscosity test is very sensitive

³⁴ H. Staudinger and I. Jurisch, *Papier-Fabr.* 35, No. 49: 459-462 (Dec. 3, 1937)

³⁵ G. H. McGregor, *Paper Trade J.* 102, No. 11: 155-167 (Mar. 12, 1936)

³⁶ C. C. Houtz and D. A. McLean, *J. Phys. Chem.* 43, No. 2: 309-321 (Mar., 1939)

³⁷ A. J. Stamm and L. A. Hansen, *Ind. Eng. Chem.* 29, No. 7: 831-833 (July, 1937)

³⁸ J. P. Wiedner, *Paper Trade J.* 108, No. 1: 1-10 (Jan. 5, 1939)

³⁹ J. Strachan, *Paper-Maker* 111, No. 5: TS41-42 (May, 1946)

to changes in D.P., but in the low part of the viscosity range, the test is not so sensitive.⁴⁰

The viscosity test is widely used as a valuable guide for the suitability of cellulose for the manufacture of cellulose derivatives. Though not so widely used in paper manufacture, the viscosity test is useful for measuring the degradation of cellulose resulting from overcooking, overbleaching, and other degrading influences. In the case of pulps to be used for making permanent paper, the highest possible viscosity is desired.

The two principal solvents used for dissolving cellulose in the viscosity test are cuprammonium and cupriethylenediamine. Cuprammonium is the older solvent and has been used more widely, but cupriethylenediamine is simpler to use and has the advantage of forming a more stable dispersion. Cuprammonium is made from copper and ammonia, the ratio of which is standardized by TAPPI at 15 g. of copper and 200 g. of ammonia per liter. Cellulose is soluble in cuprammonium of this composition to the extent of 4 to 5%, but the standard concentration used for making viscosity tests is 1%.⁴¹ In the cupriethylenediamine method, the solvent is ethylenediamine saturated with copper hydroxide and diluted so that the copper concentration is 0.5 molar. A 0.5% solution of cellulose is recommended when a pipette is used for making the viscosity test, and a 1.0% solution is recommended for the falling ball method. Conversion tables can be used to convert from one scale to the other.

In making viscosity tests by the cuprammonium method, several precautions should be observed. The sample must be properly disintegrated, and particular care must be taken to exclude light and air from the solution. Staudinger and Jurisch⁴² found that the D.P. of cellulose dissolved in cuprammonium was lowered by one-half upon exposure of the dispersion to light for 125 hours, or upon exposure to atmospheric oxygen for 25 hours. Highly lignified fibers or fibers which have been oxidized give erroneous results. The method of making the cuprammonium viscosity test is described below.

The calculated weight of oven-dry pulp to give a 1% solution is loosely rolled into the form of a narrow cylinder in a strip of hard-surfaced paper such as glassine, then moistened with 5 or 6 drops of water, and the test sample is pushed from the paper into a viscosity tube. The cuprammonium solution is siphoned into the bottom of the tube, using a rubber tube attached to the bottom, until the tube is two-thirds full. The pulp roll is then quickly broken up with the aid of a thin glass stirring rod, the remainder of the solution is added at the top, the rod is scraped clean, and a stopper is inserted in the tube. The excess solution is forced through the capillary and the stop-

⁴⁰ H. Staudinger and F. Reinecke, *Papier-Fabr.* 36, No. 49: 489-495 (Dec. 2, 1938)

⁴¹ This is for TAPPI standard; a 2.5% solution is recommended by the American Chemical Society.

⁴² H. Staudinger and I. Jurisch, *Papier-Fabr.* 35, No. 49: 462-469 (Dec. 3, 1937)

cock is closed. The viscosity tube is wrapped in black cloth and placed in a wheel rotating at 3 or 4 r.p.m., so that a metal wedge falls freely through the solution as the tube rotates. The pulp should be well broken up before the tube is put on the rotating wheel so that the metal wedge will fall the full length of the tube. About 15 hours' rotation (overnight) will be required for the complete dispersion of the pulp. At the end of this time, the tube is placed in a thermostat at 20° C. until equilibrium is established. The rubber tubing and rubber stopper are then removed, allowing the pulp solution to flow through the capillary. The time in seconds required for the meniscus to pass between the marks on the tube is noted, and the viscosity of the solution is calculated from suitable formulae.

Generally speaking, a pulp which has a high viscosity is a pulp which has a high alpha cellulose content. It is possible, however, for a considerable decrease in viscosity to occur in the higher ranges of viscosity without any appreciable loss in alpha cellulose, but beyond a certain point, that is, about 20 cp., there is a rapid loss in alpha cellulose, with a further reduction in viscosity. Below a certain point, a loss in viscosity is reflected in a loss in fiber strength, but cellulose can be reduced in viscosity quite extensively before the strength properties of the fiber are seriously affected. Ott⁴³ reports that the strength of cellulose fibers (cotton, linen, and ramie) is not seriously affected until the D.P. is reduced below about 600.

Copper Number

The copper number is an empirical test used to measure the reducing value of cellulose. The copper number is expressed in terms of the number of milligrams of metallic copper which is reduced from cupric hydroxide to cuprous oxide in alkaline medium by a given weight, i.e., 100 g., of cellulose material. (See TAPPI Standards.) Native cellulose has a low reducing power because it contains only one reducing group for each large molecule. On the other hand, degraded cellulose has a high reducing value because of the greater number of reducing groups per unit of weight. Undegraded cotton cellulose has a copper number between 0.02 and 0.01 g., and for all practical purposes, this may be considered as zero reducing value.⁴⁴ Completely hydrolyzed cellulose, i.e., glucose, has a copper number of about 300. Between these two extremes lie the degraded cellulose products.

The copper number is determined by the number of reducing groups on the cellulose chain, as well as by the average chain length. Oxycellulose has a very high copper number, and detection of oxidation has been one of the greatest uses for the copper number. If oxidized pulp has been treated with strong alkali, however, as, for example, during the alkaline purification

⁴³ E. Ott, *Ind. Eng. Chem.* 32, No. 12: 1641-1647 (Dec., 1940)

⁴⁴ C. G. Schwalbe, *Z. angew. Chem.* 37: 125 (1924)

of pulp, the copper number is no longer a reliable indication of oxidative degradation.⁴⁵

Alkali Solubility

For some purposes, it is useful to determine the amount of degraded cellulose present in a given sample of pulp. The test most widely used for this purpose is the 1% alkali solubility test. It would, of course, be possible to use a test based upon the solubility in 2, 3, or 4% sodium hydroxide solution, but on account of its rather wide use, the 1% solubility test has come to have a certain significance in pulp testing. In carrying out this test, a disintegrated sample of pulp is digested in 1% sodium hydroxide at 97 to 100° C. for exactly 1 hour, stirring at three different intervals during this period. The test is useful for measuring the amount of degraded substances which are present in pulp after pulping and bleaching. A marked rise in the 1% alkali solubility after bleaching is indicative of overbleaching.

Electrokinetic Potential of Cellulose

One of the important properties of cellulose is its ability to take on a negative electrokinetic potential, a zeta potential, when suspended in water or dilute salt solution. The potential for the cellulose-water interface has been reported by McKinley and Gortner⁴⁶ as -5.8 mv. and by Briggs⁴⁷ as -20 mv. for filter paper and -8 mv. for wood pulp (sulfite). In non-polar liquids such as benzene, the potential is zero.

The ability of cellulose to take on a negative charge is related to the presence of hydroxyl groups and is probably caused by the existence of a positive residual valency which results in the adsorption of negative ions. At low concentrations, most monovalent cations increase the negative charge,^{48, 49} but nearly all ions decrease the negative charge when present in high concentrations, i.e., over about 1×10^{-4} N. The effect of ions is greater the higher the valency of the ion. Hydrogen ion decreases the negative charge until an isoelectric point is reached at a pH of 2.0 to 3.0.^{50, 51}

The electrokinetic potential is an important factor in the swelling of cellulose fibers in water, the greatest swelling occurring at the highest potential. It is important in sheet formation and is also a factor in the retention of starches, rosin size, pigments, dyestuffs, wet-strength resins, and other similar materials added to the papermaking furnish.

⁴⁵ D. A. Clibbens, A. Geake and B. P. Ridge, *J. Textile Inst.* 18: 278 (1927)

⁴⁶ M. W. McKinley and R. A. Gortner, *J. Phys. Chem.* 34: 1509-1539 (1930)

⁴⁷ D. R. Briggs, *J. Phys. Chem.* 32: 641-646 (1928)

⁴⁸ D. R. Briggs, *J. Phys. Chem.* 32: 641-646 (1928)

⁴⁹ A. J. Stamm, "Colloid Chemistry of Cellulosic Materials," *U. S. Dept. of Agri., Misc. Publ.* 240 (1936)

⁵⁰ A. M. Sookne and M. Harris, *J. Research, Natl. Bur. Standards* 26, No. 1: 65-69 (Jan., 1941)

⁵¹ S. M. Neale and R. H. Peters, *Trans. Faraday Soc.* 41: 478 (1946)

Ion Exchange

If acid-washed cellulose fibers are treated with a salt such as sodium chloride, there is an interchange of ions whereby the cellulose takes on sodium ions and liberates hydrogen ions.⁵² The exchange capacity of naturally occurring cellulose fibers decreases as the purity of the fibers is increased, indicating that most of the exchange capacity is due to impurities in the fiber. However, even highly purified fibers exhibit some exchange capacity, owing in all probability to the presence of a small number of carboxylic acid groups in the cellulose molecule.

Among the materials to which the exchange capacity of commercial pulps has been attributed are the beta and gamma celluloses, lignin, and pectic substances. Acidic groups (e.g., carboxyl, sulfonyl, and phenolic hydroxyl groups) present in these non-cellulosic residues are believed to be the primary points at which the exchange reactions take place.⁵³ A high exchange capacity appears to be related to a high ash content.^{53, 54}

Theoretically, any cation may be held by cellulose, but cations of high valence are held with greater tenacity than cations of low valence, although hydrogen ions are strongly held by some pulp fibers. Aluminum ion, obtained from the alum added in the papermaking process, is strongly and selectively adsorbed by pulp fibers, probably by ion exchange.⁵⁵⁻⁵⁷ Iron is another material strongly adsorbed, although probably the mechanism is one of adsorption rather than true ion exchange. Ferric iron seems to be most strongly adsorbed in highly acid medium (pH 2.5 to 3.0), whereas ferrous iron is best adsorbed in mildly acid medium (pH 4.0 to 5.5).⁵⁸ Adsorption of iron causes discoloration of pulp fibers and is a cause for concern whenever water of high iron content is used.

Alkali Adsorption

Cellulose fibers have a tendency to adsorb alkali from solution. Commercial pulps of low purity, i.e., unbleached pulps, have a stronger tendency to bind alkali than highly purified pulps. Hence, it is logical to assume that most of the alkali-binding property resides in the non-cellulosic constituents, but even relatively pure cellulose exhibits some alkali adsorption. In the case of relatively pure cellulose (e.g., rag pulps), the binding of alkali seems to be by sorption only, but in the case of impure pulps (e.g., un-

⁵² S. M. Neale, *Nature* 135: 583 (1935)

⁵³ D. A. McLean and L. A. Wooten, *Ind. Eng. Chem.* 31, No. 9: 1138-1143 (1939)

⁵⁴ D. A. McLean, *Ind. Eng. Chem.* 32, No. 2: 209-213 (Feb., 1940)

⁵⁵ C. G. Schwalbe, *Z. angew. Chem.* 37: 125 (1924)

⁵⁶ E. G. V. Percival, A. C. Cuthbertson and H. Hibbert, *J. Am. Chem. Soc.* 52, No. 8: 3257-3269 (Aug., 1930)

⁵⁷ H. F. Launer, *Paper Trade J.* 110, No. 10: 135-140 (Mar. 7, 1940)

⁵⁸ *J. Soc. Chem. Ind. (Japan)* 37: 89-92 (1934)

bleached wood pulps), part of the alkali is bound by a chemical combination of the alkali with the acidic constituents of the pulp.

There appears to be a relationship between the lignin content, copper number, and alkali-binding power of different pulps.⁵⁹ The pH of the pulp has no direct bearing on alkali binding, nor are the alkali-binding properties greatly affected by keeping the pulp in contact with acid solutions. Alkali binding is very important in sizing when neutral rosin size is used, since the fibers tend to remove alkali from the rosin soap and slowly force the hydrolysis of the soap to free rosin.⁶⁰

Physical Structure of Cellulose

The outstanding physical characteristic of cellulose molecules is their long chain length, which is generally believed to be in the neighborhood of 500 to 1,000 Å. The width of the molecules is generally considered to be about 9 Å. and the thickness about 4.7 Å. It is the chain-like structure of the individual molecules which imparts tensile strength to the fibers, since tensile strength increases approximately linearly with an increase in the degree of polymerization.

If the primary valence bonds in a cellulose fiber were continuous, Mark⁶¹ calculates that the fiber would have a tensile strength of 800 kg./sq.mm. (0.8 g./sq. micron), which Clark⁶² estimates as equivalent to a tensile strength of 130 g. for the average spruce sulfite fiber having a cross-sectional area of about 160 sq. microns. This is an exceedingly high tensile strength, equivalent to the strongest metals. Actually, the average paper-making fiber obtained from wood has a tensile strength in the neighborhood of about 10 g.^{63, 64} which, while still very high, is far short of the theoretical value predicted above. The tensile strength of individual cellulose fibers, expressed in terms of breaking length, i.e., the length required to cause rupture under its own weight, has been reported to be about 23,000 m.⁶⁵ (for cotton) and 40,000 m.⁶⁶ (for wood fibers).

Crystalline and Amorphous Cellulose

The reasons for the lower-than-theoretical values for fiber strength

⁵⁹ M. L. Downs, *Paper Trade J.* 107, No. 16: 184-188 (Oct. 20, 1938)

⁶⁰ B. W. Rowland, *Paper Trade J.* 101, No. 13: 98-100 (Sept. 26, 1935)

⁶¹ H. Mark, *Melliand Textilber.* 10: 695-700 (1929)

⁶² J. d'A. Clark, *Paper Trade J.* 118, No. 1: 1-6 (Jan. 6, 1944)

⁶³ F. Rühlemann, Doctor's Dissertation, Dresden, Tech. Hochschule, Borra-Leipzig, Moske, 63 pp. (1935)

⁶⁴ J. d'A. Clark, *Pulp Paper Mag. Canada* 44, No. 1: 92-102, Convention Issue (1943)

⁶⁵ P. M. Hoffman Jacobsen, *Paper Trade J.* 81, No. 22: 216-217 (Nov. 26, 1925) translated from *Le Papier*

⁶⁶ W. Klauditz, A. Marschall and W. Ginzel, *Holzforschung* 1, No. 4: 98-103 (1947)

are (1) that primary valence bonds do not extend the full length of the fiber and (2) that the cellulose molecules are not arranged in the most effective fashion in the fiber. Analysis of cellulose fibers by x-ray has shown that the constituent molecules exist in a definite crystal pattern in certain regions of the fiber, referred to as the crystalline region. In other regions, however, the molecular arrangement is more random and less compact, and this is referred to as the amorphous areas. The amorphous areas vary from regions of complete randomness to regions approaching crystallinity. The ratio of crystalline to amorphous cellulose has an appreciable effect on the reactivity and the physical properties of cellulose fibers.

The amorphous material in native fibers is composed partly of non-cellulosic constituents (e.g., hemicelluloses and lignin), but as pointed out above, there is also an appreciable amount of cellulose which is in an amorphous state. It is generally believed that all cellulose as originally produced in growing plants is amorphous, but that part of the cellulose develops crystallinity as the plant matures. Berkley and Kerr⁶⁷ found that cotton fibers taken from developing bolls show little or no evidence of a crystal structure until the fibers are dried out. The removal of water from fibers in the wet condition by drying increases the amount of crystalline cellulose because of the increase in number of bonds between the hydroxyls of adjacent cellulose chains. Ritter⁶⁸ believes that the amount of crystalline cellulose in wood fibers increases until the fibers are twelve days old, after which there is no further change.

The ratio of crystalline to amorphous material in cellulose fibers can be determined (1) by chemical methods, such as by differences in rate of hydrolysis, oxidation, and acetylation in various parts of the fiber, and (2) by physical methods, which include x-ray analysis, density measurements, and moisture regain methods. The results obtained by these various methods differ rather widely. Generally, the chemical methods indicate considerably higher proportions of crystalline cellulose than the physical methods, possibly because of recrystallization during treatment. The most recent work based on physical methods of analysis indicates values of 60 to 87% for ramie, native cotton, and flax, 50 to 65% for wood fibers, and about 25 to 40% for viscose rayon.⁶⁹⁻⁷²

In the crystalline region, the fiber has its maximum strength, maxi-

⁶⁷ E. E. Berkley and T. Kerr, *Ind. Eng. Chem.* 38, No. 3: 304-309 (Mar., 1946)

⁶⁸ G. J. Ritter, "Report on Wood Chemistry Meeting," *Paper Ind.* 29, No. 7: 998, Oct., 1947

⁶⁹ E. Heuser, *Tappi* 33, No. 3: 118-124 (Mar., 1950)

⁷⁰ P. H. Hermans, *Contribution to the Physics of Cellulose Fibres*, p. 71. Elsevier Publ. Co., Inc., New York, N. Y. (1946)

⁷¹ TAPPI Monograph No. 6: "Nature of the Chemical Components of Wood." P. 20. Tech. Assoc. of the Pulp and Paper Industry, New York, N. Y. (1948)

⁷² P. H. Hermans and A. J. Weidinger, *J. Applied Physics* 19: 491 (1948)

mum resistance to swelling, and maximum resistance to elongation. The tensile strength of crystalline cellulose has been estimated at 15 times that of amorphous cellulose, and the elastic modulus at 10^5 times that of amorphous cellulose.⁷³ In the amorphous regions, the fiber has its greatest extensibility and flexibility. Amorphous cellulose is characterized by a minimum of resistance to hydrolysis, being completely hydrolyzed by boiling in 2.5 molar hydrochloric acid for four minutes.⁷⁴ The degradation which occurs when cellulose is treated with acids or oxidizing agents is believed to occur principally in the amorphous regions.^{75, 76}

Cellulose would be water dispersible (despite its high molecular weight) if it were not for its pronounced tendency to form a rigid crystalline structure. This crystalline structure holds the individual cellulose molecules so rigidly that it is very difficult for water molecules to penetrate between the chains. If a small part of the hydroxyl groups is substituted so that the cellulose chains are pried apart, the final product is dispersible in water, because water molecules are now able to penetrate between the chains. Commercial examples of such products are methylcellulose and carboxymethylcellulose. Cellulose which has been completely substituted with non-polar substituents is no longer water dispersible, but the product is more plastic than the original cellulose because the chains are freer to slip by one another.

Unit Cell

Sponsler and Doree⁷⁷ postulated the idea of the unit cell, and later others elaborated upon its architecture. The unit cell is the geometrical pattern or arrangement of glucose units which must be repeated in all directions to produce the crystalline regions of cellulose fibers. The unit cell is not a definite physical entity, but merely a theoretical recurring spacing which contains only a part of any one cellulose molecule. According to Meyer and Mark, its shape is monoclinic. It has the general shape and dimensions represented by the following:

$$a = 8.35 \text{ \AA.}$$

$$b = 16.3 \text{ \AA.}$$

$$c = 7.9 \text{ \AA.}$$

$$\beta = 84^\circ$$

The unit cell consists of two sets of cellulose chains, both parallel to each other. Along the axis of molecule alignment, the glucose units are

⁷³ H. Mark and E. H. Freund, *Rayon Text. Monthly* 515-519 (Sept., 1942)

⁷⁴ R. F. Nickerson and J. A. Habrle, *Ind. Eng. Chem.* 38, No. 3: 299-301 (Mar., 1946)

⁷⁵ R. F. Nickerson, *Ind. Eng. Chem.* 33, No. 8: 1022-1027 (Aug., 1941)

⁷⁶ D. M. Musser and H. C. Engel, *Paper Trade J.* 114, No. 15: 173-175 (Apr. 9, 1942)

⁷⁷ O. L. Sponsler and W. H. Doree, *Col. Sym., Monograph* 4: 174 (1926)

held together by primary valence bonds which are the strongest of chemical forces. Along another axis, secondary valence forces (OH dipoles and electric moment C—O—C) act to bind the glucose units together. Along the third axis, it is now believed that the hydrogen bond is formed between oxygen atoms, causing a strong bond and tight packing. Thus, cellulose chains are held together by at least three different types of forces, and the spacing between the chains is different in the three directions.

The orientation of the molecular chains, which are nearly parallel to the length of the fiber, explains the high mechanical strength of the fiber in the lengthwise direction. In the lateral direction, the strength is lower and the fiber tends to swell more because of the relatively weak secondary valence forces holding the molecules together in this direction. However, the strength is still fairly high in this direction because the secondary valence forces make up for their inherent weakness through great numbers. Furthermore, cross linkages of primary valence bonds (e.g., half-acetals) may be present in some cases.⁷⁸ Where hydrogen bonds are in effect, the strength is quite high. According to Mark,⁷⁹ about 6,000 cal./mole are required to open a hydrogen bond in the crystalline areas.

Cellulose Crystallites

Cellulose crystallites are the regions of the cellulose fiber where the molecules are arranged in an orderly fashion, i.e., the regions where the unit cell prevails. Originally, crystallites were regarded as fundamental units (micelles) beyond which there could be no further subdivision, but recent evidence indicates that the crystallites are incidental units which vary in dimensions in different fiber types and vary even in fibers of the same type if the fibers have been subjected to severe chemical and mechanical treatment.

The most commonly accepted explanation for the crystalline and amorphous areas in cellulose fibers is that the crystalline regions prevail where the cellulose molecules are lined up in parallel fashion, whereas the amorphous cellulose prevails where the molecules are randomly arranged.⁸⁰ This theory postulates that a given cellulose molecule may belong to both a crystallized and an amorphous area, and that the ordered and disordered areas are not clearly defined.⁸¹ It is believed that the long cellulose molecules protrude at the surface of the crystallites to give a fringe structure. These protruding chains permit association to take place between the cellulose and non-cellulosic constituents of the fiber, thus forming an amor-

⁷⁸ E. Heuser, *Paper Trade J.* 122, No. 3: 21-26 (Jan. 17, 1946)

⁷⁹ H. Mark, Subcommittee on Wood Chemistry, Meeting at Cleveland, Wis. (Aug. 15, 1948)

⁸⁰ H. Mark, *J. Phys. Chem.* 44, No. 6: 764-788 (June, 1940)

⁸¹ H. Mark, *Ind. Eng. Chem.* 34, No. 4: 449-454 (Apr., 1942)

phous mixture of cellulose and non-cellulosic substances, which may be held together by secondary valence forces. The whole arrangement forms a fairly strong structure, but one which has sizable regions of empty space.

Analysis by x-ray has been widely used to determine the size, shape, and geometrical position of the theoretical cellulose crystallites as they exist in the fiber. Mark and Hengstenberg⁸² estimate the length at 600 Å. and the diameter at 50 Å., and Ritter⁸³ also reports a size of $50 \times 50 \times 500$ – $1,000$ Å. Campbell⁸⁴ estimates that the crystallites average about 50 cellulose molecules in cross section. The total outside area of the crystallites is very large, and is believed to account for up to 50% of the total cellulose surface, as evidenced by the fact that there is no change in the x-ray diagram upon acetylation until more than 50% by weight of the cellulose is acetylated.⁸⁵

Unit Fibrils

Fibrils are small thread-like units which, in large numbers, make up the full-sized cellulose fiber. Originally, it was believed that the fine frayed-out ends which are visible in well-beaten pulp when examined under the optical microscope were fibrils. However, most chemists now believe that these relatively coarse fibrous units are composed of still smaller units, called microfibrils, which in turn are made up of aggregates of crystallites.

There are two principal schools of thought. One school believes that there is definite physical entity with sharply defined boundaries, called a unit fibril. Adherents of this theory feel that unit fibrils are true morphological units of uniform size which retain their structural integrity after all other fiber characteristics are lost. Another school regards the units known as fibrils as fiber elements of indefinite dimensions which depend for their size upon the method of separation. Adherents of this theory regard the fibrils as built up of crystalline cellulose interpenetrated with amorphous cellulose and possibly such substances as lignin, hemicelluloses, and pectins.

Much of the early investigation on fibril dimensions was done with the optical (light) microscope. This type of microscope has a limiting resolution in a range less than the dimensions of the fibrils, which caused the dimensions to appear to be close to the limiting resolution of the microscope. This fact leaves the earlier work on fibril dimensions open to considerable question. Some of the early investigators reported diameters in the neighborhood of 0.1 to 0.95 micron.⁸⁶⁻⁹¹ Strachan⁹² describes fibrils

⁸² J. Hengstenberg and H. Mark, *Z. Krist.* 69: 271–284 (1928)

⁸³ G. J. Ritter, *Paper Trade J.* 101, No. 18: 264–272 (Oct. 31, 1935)

⁸⁴ W. B. Campbell, *Paper Trade J.* 125, No. 19: 84–86 (Nov. 7, 1947)

⁸⁵ *Am. Dyestuff Rptr.* 25, No. 16: 423 (1936)

⁸⁶ S. H. Clarke, *Paper-Maker* 110, No. 6: TS53–54 (Dec., 1945)

⁸⁷ R. O. Herzog, *Papier-Fabr.* 23: 121–122 (1925)

as being 0.1 to 0.5 micron in diameter, but points out that these are, in turn, built up of microfibrils variable in size, but averaging about one-fifth to one-tenth the size of the fibrils. Recent work with the electron microscope indicates the presence of very small fibrils having diameters of 50 to 100 Å., and even less,⁹³⁻⁹⁶ depending somewhat upon the source of the cellulose. These sizes are open to some criticism since a size of 50 Å. is approaching the limiting resolution of the electron microscope. These dimensions approach the size of the hypothetical cellulose crystallites. Clark⁹⁷ speaks of microfibrils 0.002 micron in diameter.

The crystallites making up the fibril are arranged parallel to the long axis of the fibril. The fibrils themselves do not lie parallel to the fiber axis but are inclined at an angle which varies in fibers from different sources and which varies in different layers of the same fiber. In cotton, the fibrils are arranged with the long axis at an angle to the fiber axis forming a spiral arrangement. In ramie and linen, the fibrils are nearly parallel to the fiber axis. In wood, they form almost a right angle with the fiber axis in the outside layers of the fiber wall, and in the inside layers are arranged at angles which vary from about 10 to 30°, depending upon the species.

Morphological Structure of Cellulose

Cotton fibers are a purer form of cellulose and have a simpler morphological structure than wood cellulose. They consist of a wall which surrounds a central cavity, called the lumen. The wall consists of a secondary part and an outside or primary part, sometimes called the cuticle. The secondary wall is practically pure cellulose and is composed of several lamellae which have been estimated at 0.4 micron or less in thickness.⁹⁸ The primary wall is very thin and contains wax and pectic substances, as well as cellulose. Cotton fibers which reach the paper mill in the form of rags have had their primary wall removed by previous processing.

The areas in wood fibers may be reduced to two principal regions: the middle lamella, or intercellular region, and the cell proper, which is composed of a primary wall, secondary wall, and the lumen, or cell cavity. The

⁸⁸ E. Heuser, *Paper Trade J.* 101, No. 21: 303-310; No. 22: 317-323 (Nov. 21, 1935)

⁸⁹ W. L. Balls and H. A. Hancock, *Proc. Roy. Soc. (London)* 426-440 (1922)

⁹⁰ A. J. Bailey and R. M. Brown, *Ind. Eng. Chem.* 32, No. 1: 57-63 (Jan., 1940)

⁹¹ G. J. Ritter, *Paper Ind.* 16, No. 6: 178-183 (June, 1934)

⁹² J. Strachan, *Paper-Maker* 111, No. 1: TS1-2 (Jan., 1946)

⁹³ E. Heuser, *Tappi* 33, No. 3: 118-124 (Mar., 1950)

⁹⁴ B. M. Siegel, *Tappi* 32, No. 3: 109-112 (Mar., 1949)

⁹⁵ W. G. Kinsinger and C. W. Hock, *Ind. Eng. Chem.* 40: 1711 (1948)

⁹⁶ B. M. Siegel, *Tappi* 32, No. 3: 109-112 (Mar., 1949)

⁹⁷ J. d'A. Clark, *Proc. Tech. Section, Paper Makers' Assoc. Gt. Britain Ireland* 24: 30-54 (Dec., 1943)

⁹⁸ S. H. Clarke, *Paper-Maker* 110, No. 6: TS53-54, 61-63 (Dec., 1945)

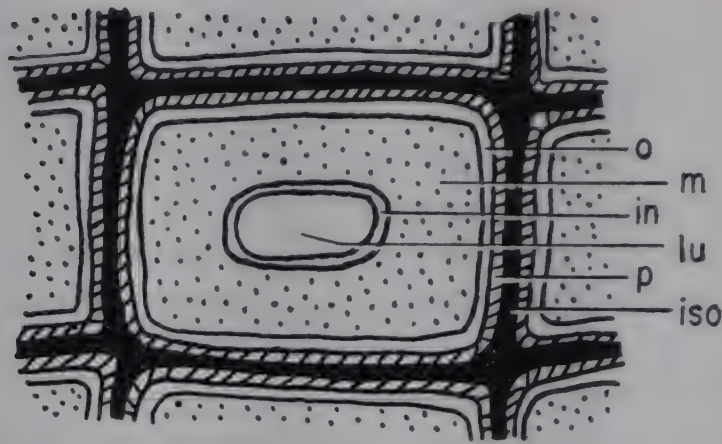


Fig. I-2. Cross section of a wood fiber with adjoining areas: (o) outer layer, secondary wall; (m) middle layer, secondary wall; (in) inner layer, secondary wall; (lu) lumen; (p) primary wall; (iso) isotropic intercellular substance.

middle lamella is composed of isotropic substance, principally lignin. The primary wall and the secondary wall contain mostly cellulose and hemicellulose, together with some lignin. Three layers of the secondary wall are recognized—the inner, middle, and outer layers. A sketch of a cross section of a wood fiber, together with the adjoining areas, is shown in Figure I-2. The distribution of the diverse chemical elements in a wood fiber is important, and the location of the major constituents of wood is discussed further in the following sections. The following percentages by volume represent typical values for a spruce fiber.

Cellulose nucleus	44.4%
Cellulose-hemicellulose	12.8%
Hemicellulose-lignin	33.05%
Lignin layer	9.75%

True Middle Lamella

The true middle lamella is the intercellular material which is shared by the adjacent cells in wood. It forms a network which completely surrounds each cell and is continuous throughout the wood structure.⁹⁹ The middle lamella contains the greatest part of the lignin in the wood, and since practically no cellulose is present in this region, it is a truly amorphous (isotropic) area. The principal functions of the middle lamella are to hold the fibers together and to confer strength and rigidity to the wood. From a papermaking standpoint, it is valueless.

Compound Middle Lamella

Of more significance to the papermaker is the “compound middle lamella.” This comprises the true middle lamella, plus the adjacent primary walls of the contiguous cells. The “compound middle lamella” is heavily

⁹⁹ A. J. Bailey and T. Kerr, *J. Arnold Arboretum* 15: 327-349 (1934)

lignified, and it, together with the outer parts of the secondary wall, account for practically all the lignin in the wood. Bailey¹⁰⁰ found that the compound middle lamella contains about 71% lignin, about 14% pentosans, and only about 4% cellulose. Recent work by Lange in Sweden, using a method of analysis based upon ultraviolet absorption, showed it to contain about 70% lignin.

Primary Wall

The primary wall is a continuous, fairly elastic membrane around the outside of the fiber. It forms only a small part of the fiber, being only about 0.5 micron in thickness, but since it surrounds the fiber, it greatly influences the surface properties. Upon pulping and bleaching, the fiber loses most of its primary wall, and that which remains becomes quite inelastic.

The chemical constitution of the primary wall is not well known. Crystalline cellulose is present, but a high percentage of non-cellulosic matter is also present, and for this reason, the primary wall is classified as isotropic. The fibrils which are present appear to be arranged at random.

The primary wall is less heavily lignified than the outer layer of the secondary wall,¹⁰¹ but it is so heavily lignified in mature plants that it is difficult to distinguish between it and the middle lamella, and for this reason, the two regions are referred to as the "compound middle lamella." In some methods of delignification, the primary wall is the last to give up its lignin. Hemicelluloses and pectic substances are present in the primary wall. There is recent evidence of mannan.

The typical "ballooning" which occurs when pulp fibers are suspended in cuprammonium is believed to be caused by the fact that the primary wall of the fiber does not swell appreciably in this solvent, whereas the secondary wall swells greatly, thereby resulting in a distortion of the outside layer.^{102, 103} The primary wall apparently acts as a semipermeable membrane through which the cuprammonium hydroxide diffuses and combines with the underneath cellulose. Since the cellulose-copper complex cannot diffuse back through the wall, an osmotic pressure is built up which expands the fiber. Highly lignified, virgin fibers do not balloon in cuprammonium unless the outer protective layer is ruptured.

Secondary Wall

The secondary wall of wood fibers constitutes the major portion of the wall of most cell types. The thickness varies considerably, depending upon

¹⁰⁰ A. J. Bailey, *Ind. Eng. Chem., Anal. Ed.* 8, No. 1: 52-54 (Jan., 1936)

¹⁰¹ A. L. M. Bixler, *Paper Trade J.* 107, No. 15: 171-182 (Oct. 13, 1938)

¹⁰² F. E. Brauns and H. F. Lewis, *Paper Trade J.* 105, No. 10: 141-143 (Sept. 2, 1937)

¹⁰³ H. F. Lewis and C. A. Richardson, *Paper Trade J.* 109, No. 14: 188-190 (Oct. 5, 1939)

the type of cell, but in general, the secondary wall is a relatively thick layer. It is bordered on the outside by the relatively thin primary wall and on the inside by the lumen or central cavity of the fiber.

The secondary wall of wood fibers contains cellulose, hemicelluloses, and lignin, and is anisotropic. It is composed of a matrix of highly oriented fibrils interpenetrated by the non-cellulosic constituents of the fiber. The wall is often pitted and cracked and, in addition, some woods (notably Douglas fir) have spiral thickenings on the inner surface next to the lumen. The secondary wall is comparatively elastic compared with the inelastic primary wall and tends to swell appreciably in cooking liquors and in the presence of swelling agents.¹⁰⁴

The secondary wall is noticeably laminated into layers which differ in composition and arrangement of fibrils. Usually, three distinct zones are recognized and, in some cases, even more. Each layer has its particular function. The outer layer next to the primary wall contains the highest percentage of lignin and serves primarily to hold the inner layers intact. It is likely that the cellulose in this outer layer has a shorter chain length than the cellulose in the inner layers. During pulping, this cellulose is further degraded, and in alkaline pulping, a considerable amount of the short-chain material is probably removed. The primary function of the inner layers of the secondary wall is to provide longitudinal strength to the fiber. In thick-walled cells, the inner layers are greatly enlarged. In the outer and the inner layers of the secondary wall, the fibrils are wound at approximately right angles to the fiber axis, whereas in the center layer, the fibrils are wound at a smaller angle, usually from 10 to 30°.

Submicroscopic Pore Structure of Cellulose Fibers

A cellulose fiber may be visualized as a structural unit consisting of the unit cell, the crystallites, microfibrils, and fibrils. Recent theory favors regarding these units not as discrete areas, but rather as parts of a continuous system of overlapping chain molecules. The whole fiber may be regarded as a porous medium with a gradation in the space system ranging from botanical capillaries down to colloidal structures.^{105, 106} The system is intercommunicating, and any material penetrating the fiber can shift from one path to another, following a devious path. It is estimated¹⁰⁷ that a molecule passing through the cell wall in the fiber direction must shift from one path to another on the average of about 12.5 times. The system is complicated by the presence of non-cellulosic materials, i.e., hemicelluloses, lig-

¹⁰⁴ W. M. Harlow, *Paper Trade J.* 109, No. 18: 242-246 (Nov. 2, 1939)

¹⁰⁵ W. W. Barkas, *Proc. Phys. Soc. (London)* 48: 576-588 (1936)

¹⁰⁶ J. Strachan, *Paper-Maker* 111, No. 1: TS1-2 (Jan., 1946)

¹⁰⁷ A. J. Stamm, *Tappi* 32, No. 5: 193-199 (May, 1949)

nin, pectins, etc., which form a continuously interlocking and interpenetrating system in certain regions of the cellulose.

In general, two distinct pore systems are recognized, the microscopic (or gross) pores and the submicroscopic (or molecular) pores. The latter (submicroscopic) may be present¹⁰⁸ as: (1) gaps in the cellulose crystallites, (2) gaps due to lack of orientation between parallel or nearly parallel crystallites, (3) gaps due to layers of crystalline material passing each other at an angle, and (4) gaps where non-cellulose material is included.

The size of the submicroscopic pores has been estimated at from 10 to 1,000 Å.^{109, 110} The smallest have been estimated as equivalent to a circular opening about 5 to 10 Å. units in diameter, a size about 1/30,000 of the diameter of the fiber.¹¹¹ During swelling, the size of these pores increases, and they may then average about 50 to 200 Å.¹¹²

Water can penetrate into the pores of the fiber and even gradually get between the cellulose chains, an important factor in swelling phenomena, as will be explained later. Small molecules of dispersed materials can also penetrate into these pores, an example being the flameproofing of cotton fabric by the use of soluble tin salts which penetrate into the pores of the fiber and are precipitated there by the action of diffusible ions. However, most of the adjuncts of papermaking are too large in size to penetrate into the submicroscopic pores of the fiber, although certain dyestuffs and low molecular weight water-soluble resins are able to do so. Many of the adsorption reactions and ion exchange properties attributed to cellulose fibers take place within the pore structure.

Specific Surface

Because of its submicroscopic pore structure and general colloidal nature, cellulose fibers present a tremendous surface area. The pore space in cotton fibers has been estimated at 35 to 40% of the fiber volume.

The total surface area of cellulose fibers is referred to as the total specific surface, a term which may be defined as the total surface area involved in adsorption and absorption phenomena. The total specific surface may be subdivided into external (microscopically visible) surface and internal (submicroscopic) surface.

The external surface includes the outside area of the fiber, as well as the area within the coarse fiber cavities. The external surface may be measured by microscopic methods, silvering technique, adsorption methods using non-polar compounds, and permeability methods. Values for un-

¹⁰⁸ W. B. Campbell, *Tappi* 32, No. 6: 265-271 (June, 1949)

¹⁰⁹ O. Kratky and F. Schosberger, *Z. physik. Chem.* B39: 145-154 (Apr., 1938)

¹¹⁰ S. H. Clarke, *Paper-Maker* 110, No. 6: TS53-54, 61-63 (Dec., 1945)

¹¹¹ A. M. Schwartz, *Am. Dyestuff Reprtr.* 33, No. 8: 164 (1944)

¹¹² A. M. Schwartz, *Am. Dyestuff Reprtr.* 33, No. 8: 164 (1944)

beaten fibers range from about 2×10^3 to 1.5×10^4 cm.²/g. (See Chapter VI, "Fiber Preparation.") Beating or other mechanical treatment of the fiber greatly increases the amount of external surface.

The internal surface of the fiber is composed of the surface present in the submicroscopic pores which exists in the presence of swelling agents (e.g., water and aqueous solutions). The amount of internal surface is not appreciably affected by mechanical treatment of the fiber, i.e., by beating, but it is greatly affected by the type of swelling agent used. The internal surface of dry fibers is approximately 8×10^4 cm.²/g., compared with about $3\text{--}5 \times 10^6$ cm.²/g. in the presence of strong swelling agents.¹¹³⁻¹¹⁵ The latter is close to the theoretical value predicted from the crystalline nature of cellulose.¹¹⁶ It can be seen that the internal surface is approximately 100 to 1,000 times greater than the external surface.

Adsorption and Swelling of Cellulose

Cellulose is a gel and, as such, adsorbs gases, liquids, and solids. Cellulose has a high degree of molecular cohesion but, if the penetrating agent is strongly polar in nature, swelling of the fibers results. There are two types of swelling, namely, swelling of the crystallites and swelling of the intercrystalline regions depending upon whether the swelling agent penetrates into the crystallites or only into the intercrystalline regions. Cellulose having the highest percentage of amorphous material exhibits the greatest amount of swelling, since water preferentially enters the amorphous regions. Water can also penetrate the crystalline areas but it does not affect the spacings in these areas.

Sorption of Gases and Liquids

As an illustration of the adsorption of gases by cellulose, it has been shown that about 0.023 cc. of air is adsorbed per gram of cotton fiber,¹¹⁷ and that about 0.126 cc. of nitrogen is adsorbed per gram of paper.¹¹⁸ Polar gases (e.g., sulfur dioxide, ammonia, and carbon dioxide) are adsorbed to a greater extent than non-polar gases. Thus, Grace and Maass¹¹⁹ found that wood adsorbs over 13% sulfur dioxide compared with only 1% carbon dioxide. In the same connection, Rowen and Blaine¹²⁰ found that the

¹¹³ A. J. Stamm and M. A. Millet, *J. Phys. Chem.* 45: 43 (1941)

¹¹⁴ A. G. Asaf, R. H. Haas and C. B. Purves, *J. Am. Chem. Soc.* 66: 59 (1944)

¹¹⁵ W. B. Campbell, *Canadian Dept. Interior, Forest Service Bull.* 84 (1933)

¹¹⁶ C. A. Harris and C. B. Purves, *Paper Trade J.* 110, No. 6: 63-67 (Feb. 8, 1940)

¹¹⁷ G. F. Davidson, *J. Textile Inst.* 18: T175 (1927)

¹¹⁸ P. H. Emmett and T. DeWitt, *Ind. Eng. Chem., Anal. Ed.* 13, No. 1: 28-33 (Jan., 1941)

¹¹⁹ N. H. Grace and O. Maass, *J. Phys. Chem.* 36, No. 12: 3046-3063 (Dec., 1932)

¹²⁰ J. W. Rowen and R. L. Blaine, *Ind. Eng. Chem.* 39, No. 12: 1659-1663 (Dec., 1947)

surface area of cellulose fibers is 150 to 200 greater when determined by water adsorption than when determined by nitrogen adsorption, due to the greater swelling which occurs in water.

The effect of polarity of liquid on adsorption has been shown by Sheppard and Newsome¹²¹ who obtained the following values using cotton linters:

Substance	Per cent sorbed
Butyl alcohol	1.5
Propyl alcohol	5.0
Ethyl alcohol	8.6
Methyl alcohol	11.2
Water	15.0

Sorption of Water

Cellulose has a very strong affinity for water. In fact, absolutely dry cellulose is one of the most hygroscopic substances known, and it will take up moisture from nearly all known drying agents, including phosphorous pentoxide. The amount of water held at equilibrium depends upon the purity of the cellulose and the humidity of the atmosphere. For most commercial pulps, the moisture content ranges from 15 to 30% in a saturated atmosphere, and from 10 to 12% under normal atmospheric conditions. The hemicelluloses and degraded celluloses are slightly more hygroscopic than true cellulose, and hence fibers which contain a high percentage of these impurities generally have a higher moisture content than highly purified fibers.

Cellulose fibers take up water by true adsorption, indicating that no compounds are formed between cellulose and water. The cellulose-water relationship can be represented by the Freundlich adsorption isotherm $\alpha = Ap^{1/n}$, where p is the equilibrium vapor pressure and α is the weight of vapor adsorbed.¹²² Water is sorbed by cellulose with a high heat of sorption, which decreases as the amount of moisture in the fiber is increased. The heat of sorption is in the neighborhood of 250 cal./g. at zero moisture content and decreases to zero calories at the fiber saturation point. Water may be held in the cellulose fiber structure as colloidal (bound) water, as capillary water, or as imbibed water. These various forms of water are discussed below.

Colloidal Water. Colloidal or bound water is water held by adsorption on the surfaces of the cellulose crystallites. Up to 3 to 4% water is

¹²¹ S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.* 36: 2306 (1932)

¹²² C. C. Houtz and D. A. McLean, *J. Phys. Chem.* 43, No. 2: 309-321 (Mar., 1939)

held in this fashion. This water is so strongly held that it no longer exhibits the properties of "free" water: for example, it has an abnormally high density; it does not freeze at normal temperatures; it cannot act as a solvent; it is not readily responsive to humidity changes; it cannot be completely removed except at very low vapor pressures. Even fibers which have been dried to constant weight in an oven at 100° C. still retain between 0.5 to 1.0% of colloidal water.

Colloidal water causes swelling of the fiber and profoundly influences the physical properties. In the beginning of the sorption process, a contraction of the fiber takes place, which is indicative of the strong association between the cellulose and the water.¹²³ This may be explained by the formation of hydrogen bonds between the water molecules and the hydroxyl groups of the cellulose. Swelling immediately follows this adsorption of water, thereby opening up new areas between the crystallites where more water can enter. The fiber volume increases during the swelling process, but the total final volume is less than that of the original solid plus the water.

Capillary Water. Capillary water is the water in excess of the colloidal water which is present in the narrow capillaries of the fiber. This water is not adsorbed but simply fills in the pores.

Capillary water retains its liquid properties and further differs from colloidal water in having less influence on the swelling or on the physical properties of the fiber. Unlike the colloidal water, it is readily responsive to humidity changes.

Capillary water can be derived from imbibed liquid water or from water vapor which has condensed in the narrow capillaries of the fiber by a process known as capillary condensation. There is no sharp transition in the absorption of colloidal and capillary water, as shown by the fact that smooth sorption curves are obtained.

According to one theory, monomolecular adsorption of water occurs up to the point of inflection of the sigmoid sorption curve (see Figure I-3), after which capillary condensation becomes predominant.

Imbibed Water. After cellulose fibers have taken up all the moisture they can from saturated water vapor, they will still absorb a large volume of water—up to 200 to 300% of the fiber weight if placed in contact with water in the liquid phase. Water absorbed this way is sometimes called imbibed water. This water goes simply to fill in the lumen and coarse visible pores of the fiber and remains there as free water. Thus, imbibed water constitutes that part of the water present in excess of the water required to fill the submicroscopic pores of the fiber.

¹²³ C. O. Seborg, F. A. Simmonds and P. K. Baird, *Paper Trade J.* 107, No. 19: 223-228 (Nov. 10, 1938)

When the pores of the fiber become filled, a sharp transition takes place in the manner of water absorption, because from this point on, additional water is taken up by simple imbibition without any swelling or other significant changes in the fiber properties. The point at which this occurs is referred to as the fiber saturation point.

At the fiber saturation point, a sharp transition occurs in the relationship between heat of swelling versus moisture content and strength of fiber versus moisture content. This fact makes it possible to calculate the fiber saturation point by extrapolation of appropriate curves back to zero heat of swelling or zero shrinkage. The saturation point varies with different fibers, but ranges from approximately 16 to 31% for cotton^{124, 125} and from 25 to 30% for wood cellulose.¹²⁶

Hysteresis in Moisture Absorption

Cellulose fibers absorb or desorb water vapor until they reach a state of equilibrium with the surrounding atmosphere. Under ordinary circumstances, commercial cellulose absorbs water from the atmosphere to a moisture content of 6 to 10%, but the exact moisture content depends upon the relative humidity of the atmosphere, the condition of the cellulose, and the previous history of the cellulose.

If a given sample of cellulose approaches equilibrium from a high humidity, it will have a higher moisture content than if it approached equilibrium from a low humidity; in other words, the equilibrium moisture content of the cellulose will be higher on desorption than on absorption. This phenomenon, which is inherent in all cellulose, is known as hysteresis. Hysteresis is illustrated by the typical water sorption isotherms for cellulose shown in Figure I-3.¹²⁵

Urquhart¹²⁷ attributed sorption hysteresis to the secondary valence bonds that are formed between adjacent hydroxyl groups when wet native cellulose is dried. In the water-filled condition, water molecules are present in both the amorphous and crystalline regions,¹²⁸ and many of the potential fiber bonds are satisfied by water. When the cellulose is dried, nearly all the water-to-cellulose bonds are replaced by cellulose-to-cellulose bonds. Upon rewetting, water-to-cellulose bonds are reestablished, but part of the previously established cellulose-to-cellulose bonds remain, thus reducing sorbed water. Within limits, the higher the initial moisture of the cellulose before drying, the greater the spread between the adsorp-

¹²⁴ J. Strachan, *Paper-Maker* 61, No. 2: 13-14 (Feb., 1946)

¹²⁵ A. R. Urquhart and A. M. Williams, *J. Textile Inst.* 15: 138-530 (1924); 16: 155 (1925)

¹²⁶ J. Strachan, *Paper-Maker* 61, No. 2: 13-14 (Feb., 1946)

¹²⁷ A. R. Urquhart, *J. Textile Inst.* 20: T125 (1929)

¹²⁸ V. J. Frilette, J. Hanle and H. J. Mark, *J. Am. Chem. Soc.* 70: 1107 (1948)

tion and desorption curves. Thus, wood pulp which has never been dried has a higher moisture content at equilibrium than the same pulp which has been dried and rewetted.¹²⁹

Sorption of water by cellulose is an exothermic process and hence is inhibited at high temperatures.^{130, 131} The reduction in amount of water sorbed varies from 0 to 1% for each degree centigrade rise in temperature between 10 to 50°. ¹³² Ulm¹³³ found, however, that the equilibrium moisture content passes through a minimum at about 21° C. under conditions of high humidity. Aiken¹³⁴ found that under certain conditions the amount of water absorbed is less below about 38° C. than it is at higher temperatures.

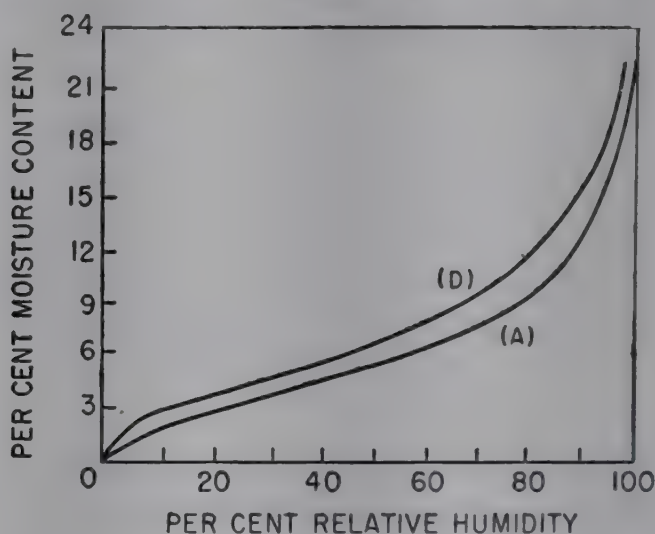


Fig. I-3. Water sorption isotherms for cellulose (kier boiled cotton): (D) desorption; (A) adsorption.

However, under most conditions, a linear relationship is obtained between the logarithm of the equilibrium vapor pressure and the reciprocal of the absolute temperature at a given moisture content.¹³⁵ Darling and Belding¹³⁶ found that the velocity of moisture adsorption is changed about 1.6-fold per 10° F. change in temperature.

Effect of Water on Fiber Properties

Water has a profound influence on the physical properties of cellulose fibers. Increasing the moisture content increases the lateral swelling, ten-

¹²⁹ C. O. Seborg, F. A. Simmonds and P. K. Baird, *Paper Trade J.* 107, No. 19: 223-228 (Nov. 10, 1938)

¹³⁰ R. W. K. Ulm, *Paper Trade J.* 106, No. 8: 71-75 (Feb. 24, 1938)

¹³¹ J. G. Wiegerink, "The Drying of Textiles," Text. Research Inst., Inc., New York, N. Y. (1944)

¹³² A. R. Urquhart and A. M. Williams, *J. Textile Inst.* 15: T559 (1924)

¹³³ R. W. K. Ulm, *Paper Trade J.* 106, No. 8: 71-75 (Feb. 24, 1938)

¹³⁴ W. H. Aiken, *Paper Trade J.* 125, No. 14: 153-157 (Oct. 2, 1947)

¹³⁵ A. C. Walker, *Textile Research* 13: 15 (1943)

¹³⁶ R. C. Darling and H. S. Belding, *Ind. Eng. Chem.* 38, No. 5: 524-529 (May, 1946)

sile strength, plasticity, and elasticity of the fibers, but decreases the rigidity. The general stress-strain relationships of a wet and a dry cellulose fiber are shown in Figure I-4.

One characteristic of cellulose fibers is that they swell appreciably in width, but very little in length. For example, a spruce sulfite fiber increases about 10% in diameter, but only about 1% in length when the relative humidity is increased from 0 to 95%. When fully saturated with water, the diameter may increase up to 20%.¹³⁷ The effects of moisture on the dimensions of cotton fiber are shown in Fig. I-5.¹³⁸ The difference in expansion in the lengthwise and crosswise directions can be attributed to the highly organized nature of cellulose fibers resulting from the orientation of the crystallites and fibrils in predominantly the same direction as the fiber axis. Since water penetrates fairly readily between the crystallites (and only with

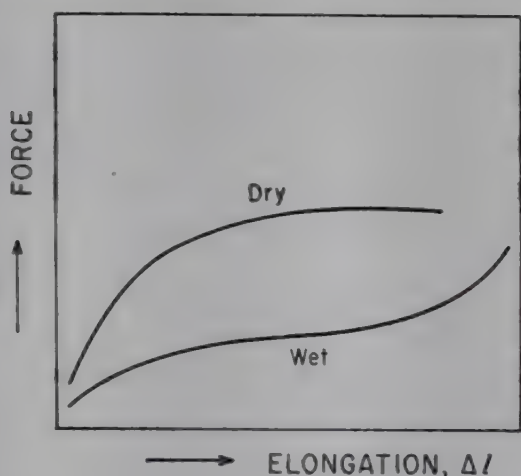


Fig. I-4. Stress-strain relationships of dry and wet cellulose fibers.

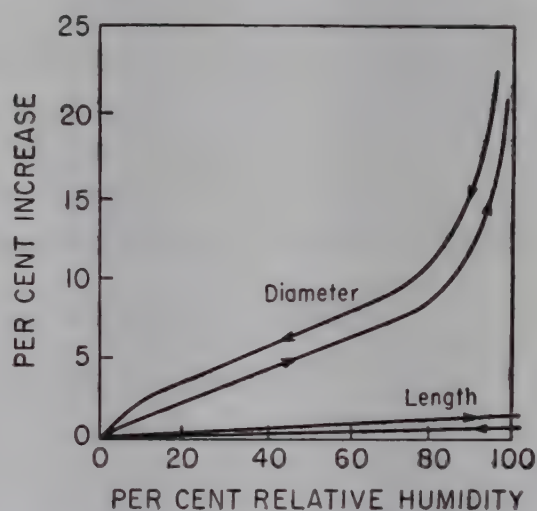


Fig. I-5. Effect of moisture on the dimensions of a cotton fiber on absorption and desorption of water.

difficulty into the crystallites), it pushes these units apart in a lateral direction, but causes practically no longitudinal expansion. The volume of expansion varies approximately linearly with the volume of water absorbed up to the fiber saturation point.¹³⁸

The tensile strength of individual cellulose fibers is increased by increased moisture content (up to a moisture content roughly equivalent to 60% relative humidity). The increased tensile strength is attributed to the fact that moist fibers permit more uniform distribution of the forces within the fiber, that is, the fibrils can straighten out and can more uniformly absorb any strain.

Bleaching of the fiber reduces the affinity for water, whereas soaking in hot water increases it. The latter is due to the release of strains and the

¹³⁷ J. P. Weidner, *Paper Trade J.* 108, No. 1: 1-10 (Jan. 5, 1939)

¹³⁸ G. E. Collins, *J. Textile Inst.* 21: T311 (1930)

freeing of more cellulose —OH groups from H-bonding. The degrading effect of overdrying on the properties of cellulose fibers has already been mentioned.

There are two methods of determining the moisture content of pulp, oven drying and toluene distillation. In the oven-drying method, the samples are dried in the oven at 105° C. until they reach constant weight. After drying, the samples are allowed to cool in a desiccator before weighing. Covers must be tightly in place during the cooling, and the sample must not be left in the desiccator any longer than necessary. Results are reported in percentage of oven-dry fiber. Drying in a vacuum oven at 50 to 60° C. is recommended for very accurate work. This gives better results than regular oven drying, because the final weight in regular oven drying is dependent upon the relative humidity of the laboratory air being circulated through the oven.¹³⁹

The toluene distillation method is a rapid and accurate procedure for the determination of moisture in comparatively small laboratory samples. Since the method does not include as water any other volatile impurities such as turpentine, unless they are soluble in water, it is especially valuable for the more impure forms of commercial pulps.

Swelling of Cellulose in Salts, Acids, and Alkalies

Cellulose undergoes considerable swelling in the presence of certain salts, acids, and bases and may actually dissolve in these substances if the concentration is high enough. The extent of swelling in salts depends upon the hydration of the ion, and consequently the salts which "dissolve" cellulose are those whose ions or molecules are highly hydrated (e.g., zinc chloride and calcium thiocyanate). The influence of anions is of more importance than the influence of cations. Certain cations (e.g., calcium) tend to inhibit swelling.

Strong solutions of mineral acids (i.e., hydrochloric acid, 40%, sulfuric acid, 70%, and phosphoric acid, 85%) swell and dissolve cellulose. Some of the bases which swell cellulose are sodium hydroxide and quaternary amines having large groups attached (e.g., dimethyldibenzylammonium hydroxide). Solutions of sodium hydroxide of higher concentration than 10% produce swelling of the crystallites, as evidenced by a change in the x-ray diagram. At a concentration of about 20%, another change occurs in the x-ray diagram which many chemists attribute to the formation of a compound of cellulose and alkali of indefinite properties, called alkali cellulose. Maximum swelling in sodium hydroxide occurs in solutions of 13 to 18% concentration. Among the non-dissociated organic compounds, thiourea, resorcinol, and phenol produce marked swelling of cellulose.

Most of the solutions of salts, acids, and bases used in pulp and paper-making are not sufficiently concentrated to cause marked swelling of cellulose. In the textile industry, however, sodium hydroxide is used as a strong swelling agent in the manufacture of mercerized cotton. The concentration of sodium hydroxide used in making rayon is also sufficiently concentrated to cause swelling of the cellulose. Sulfuric acid is used as a strong swelling agent in the manufacture of parchment papers, and zinc chloride is used in making vulcanized papers. In concentrated solutions, there is some evidence of a compound formed between cellulose and zinc chloride.¹⁴⁰ Strong solutions of zinc chloride or other similar salts are used in fiber stains to expand the fiber structure and change the dyeing properties of the fiber.

Cellulose Reactions

Cellulose undergoes many typical reactions, among which may be mentioned ester formation, ether formation, and reaction with aldehydes. Some of the derivatives of cellulose are of interest to the paper chemist because of their use as adhesives, coatings, and saturants. Of further interest to the pulp chemist is the fact that increasing amounts of wood cellulose are being used in the manufacture of these derivatives. Between 85 and 90% of the rayon manufactured in the United States is made from wood pulp.

The reactive groups in cellulose consist of the hydroxyl groups (primary and secondary alcohol groups) in each individual glucose unit and the oxygen linkages between glucose units. Since there are three hydroxyl groups for each glucose unit, it is possible to obtain substitution up to the triesters or triethers. The reactions involved in substitution are heterogeneous in nature, the kinetics of the reaction being governed more by the rate of diffusion of the substituting agent than by the rate of the chemical reaction itself.

The triesters and triethers are uniform products, but in the partially substituted derivatives, the hydroxyls on the outer layers of the crystallites are probably more highly substituted than the hydroxyls within the crystallites.¹⁴¹ The properties of the final derivative are determined (1) by the type of substituting group, i.e., methyl, ethyl, acetyl, etc.; (2) by the degree of substitution, i.e., the relative number of substituted and free hydroxyl groups; (3) by the average chain length of the cellulose molecules; (4) by the uniformity of product in regard to the length of the cellulose molecules and the degree of substitution. Some degradation usually occurs during substitution, but it is possible, under carefully controlled conditions, to con-

¹⁴⁰ A. King, *Chemistry and Industry* 57, No. 8: 177-180 (Feb. 19, 1938)

¹⁴¹ I. W. Bailey, *Ind. Eng. Chem.* 30, No. 1: 40-47 (Jan., 1938)

vert cellulose into a derivative and back again to the original cellulose without changing the degree of polymerization.

The changes brought about by substitution are both chemical and physical in nature. The solubility, swelling, and plasticity of the cellulose are chiefly affected. Derivatives of a low degree of substitution are often more sensitive to water than the original cellulose and may even be dispersible in water, owing to the crystalline structure being opened up and the internal hydroxyl groups made more available to solution. In the case of derivatives having a high degree of substitution with non-polar agents, the water sensitivity is decreased, the sorption of water is decreased, and the solubility in organic solvents is increased. The plasticity is increased by the substitution of non-polar groups, because the cellulose chain molecules are pried apart, thus weakening the attraction between molecules. The greater the chain length of the substituent group, the higher the plasticity because the chains are pried farther apart.¹⁴²

Cellulose Esters

Cellulose esters constitute one of the most important classes of cellulose derivatives. The most important members of this group are cellulose nitrate and cellulose acetate, but other cellulose esters which have been prepared include the formate, propionate, butyrate, benzoate, and mixed esters, such as cellulose acetate-propionate and cellulose acetate-butyrate.

Most of the cellulose esters used commercially are the highly substituted, solvent-soluble grades. The preparation and use of these cellulose esters in the paper industry is discussed in Chapter XXIII, "Resins." Most cellulose esters show a high degree of crystallinity upon solidification a few degrees below their melting point, and hence plasticizers are generally required to improve the plasticity and flexibility.¹⁴³

Cellulose Xanthate

Cellulose xanthate (sodium cellulose dithiocarbonate) is a water-dispersible ester of dithiocarboxylic acid, $\text{HOC}(\text{SH})=\text{S}$. It is an intermediate product in the important industrial process for making viscose rayon.

The process for making viscose rayon is carried out in seven major steps which may be summarized as follows:

(1) Preparation of alkali cellulose by treating cellulose with a 17.5% solution of sodium hydroxide for 1 to 2 hours at 20° C.

(2) Pressing to remove excess alkali, shredding, and then aging the alkali cellulose for 60 to 70 hours at 20° C. During this period, the hemicelluloses are dissolved, the viscosity of the cellulose is lowered, and the reactivity is increased.

¹⁴² S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.* 39: 143 (1935)

¹⁴³ W. O. Baker, C. S. Fuller and N. R. Pape, *J. Am. Chem. Soc.* 64: 776-782 (Apr., 1942)

(3) Treatment of the alkali cellulose with 37 to 40% carbon disulfide based on the weight of the cellulose for 2 to 3 hours to produce cellulose xanthate containing about one xanthate group (—OCSSNa) for every two glucose groups.

(4) Mixing the xanthate with dilute sodium hydroxide to produce a dispersion containing about 7 to 8% cellulose.

(5) Ripening of the viscose dispersion over a period of several days. During this period, a slow aggregation of the dispersed particles takes place with a gradual loss of xanthate groups.

(6) Coagulation of the dispersion in a bath containing sulfuric acid, sodium sulfate, zinc sulfate, and glucose to produce the regenerated cellulose in film or filament form.

(7) Washing to remove impurities.

Cellulose Ethers

Among the ethers produced commercially are methyl-, ethyl-, hydroxyethyl-, and carboxymethylcellulose. Considerable work has been done on benzylcellulose, although none of this product is being produced commercially in the United States at the present time.

Cellulose ethers are made by treating cellulose with esters of inorganic acids (e.g., alkyl sulfates or alkyl chlorides) in the presence of excess sodium hydroxide. The properties of the ether depend upon the type of substituting agent and the degree of substitution. With the higher homologs, water sensitivity is reduced, moisture sorption is reduced, and the plasticity is increased. The higher the degree of substitution, the lower the softening temperature up to a minimum point; for example, ethylcellulose has its minimum softening temperature (133°C.) at a degree of substitution of 2.6 ethyl groups per glucose unit. At low degrees of substitution, cellulose ethers are highly sensitive to water, and some grades are even water dispersible, but at high degrees of substitution, the solubility in polar solvents decreases and the solubility in non-polar liquids increases. The effect of degree of substitution on the solubility of methyl- and ethylcellulose is shown in Table I.¹⁴⁴

TABLE I
EFFECT OF DEGREE OF SUBSTITUTION ON SOLUBILITY
OF METHYLCELLULOSE AND ETHYLCELLULOSE

Methoxy groups in methylcellulose	Ethoxy groups in ethylcellulose	Solubility
0.1–1.0	1.0	In aqueous alkali
1.0–2.0	1.0–1.5	In water
2.5–3.0	2.0–2.7	In polar and non-polar organic solvents
	2.7–3.0	Only in non-polar organic solvents

¹⁴⁴ L. H. Bock, *Ind. Eng. Chem.* 29, No. 9: 985–987 (Sept., 1937)

Reaction with Aldehydes

Cellulose reacts with aldehydes (e.g., formaldehyde) in acid medium and at high temperatures. Although the exact nature of the reaction between cellulose and formaldehyde is still unknown, the reaction is believed to take place between the aldehyde and two hydroxyl groups located in different cellulose chains, thereby producing cross linkages between adjacent cellulose chains.¹⁴⁵ The reaction products may be simple methylene ethers, $\text{—O—CH}_2\text{—O—}$, of cellulose,¹⁴⁶ or more complex polyoxymethylene compounds, $\text{—O(CH}_2\text{O)}_n\text{—}$.¹⁴⁷ High concentration of formaldehyde favors the formation of the latter, i.e., polyoxymethylene ether linkages.¹⁴⁷

Cellulose which has been reacted with formaldehyde has different properties from untreated cellulose, and a methylene content of only 1 to 2% is sufficient to bring about radical changes. The reacted cellulose swells less in water and aqueous alkali than the original cellulose.¹⁴⁷ Extensive reaction with formaldehyde causes complete loss of solubility in cuprammonium.^{147, 148} Kantorowicz¹⁴⁹ found that wood pulp reacted with formaldehyde in aqueous nitric acid and then dried at 120° C. is insoluble in 17% sodium hydroxide solution, compared with a 12 to 14% solubility for the original pulp. Schwenkler and Jahn¹⁵⁰ showed that extracted pentosans become insoluble upon reaction with formaldehyde, and that pulp so treated fails to form a soluble xanthate. The tensile strength and stiffness of fibers reacted with formaldehyde is greater than that of untreated fibers because of the cross linkages between adjacent cellulose chains, which diminish the tendency of the chains to slip past one another, thereby making the system more rigid.

Hemicelluloses

The hemicelluloses are the principal non-cellulosic polysaccharides present in wood. Hemicelluloses are low molecular weight compounds (4,000 to 15,000) which are distinguished from cellulose by the fact that they are (1) soluble in dilute aqueous alkali and often in boiling water (after separation from the other wood components) and (2) hydrolyzed by warm, dilute acids into simple pentose or hexose sugars. Alkali solubility has long been used as a means of defining the hemicelluloses, but there has been considerable difference in the concentration of alkali used. Ober-

¹⁴⁵ K. Gotze and A. Reiff, *Zellwolle, Kunstseide, Seide* 46: 331–335 (1941) through *C. A.* 37: 2570 (1943)

¹⁴⁶ E. Heuser, *Paper Trade J.* 122, No. 3: 21–26 (Jan. 17, 1946)

¹⁴⁷ I. J. Gruntfest and D. D. Gagliardi, *Text. J. Res.* 18, No. 11 (Nov., 1948)

¹⁴⁸ E. Heuser, *Paper Trade J.* 122, No. 3: 21–26 (Jan. 17, 1946)

¹⁴⁹ J. Kantorowicz, U. S. 2,298,260 (Oct. 6, 1942)

¹⁵⁰ J. J. Schwenkler and E. C. Jahn. Unpublished Thesis. N. Y. State College of Forestry, Syracuse, N. Y. (1948)

manns¹⁵¹ used a 6% solution of sodium hydroxide, and Thomas¹⁵² a 17.5% solution, while others use a 4% solution. It is now known that a large part of the hemicelluloses in wood are not soluble in dilute alkali unless the lignin is removed first.

The hemicelluloses in wood are composed of a number of diverse substances, but there are two principal components, the celluloses and the polyuronides.¹⁵³ Other substances included in the hemicellulose fraction of wood are gums, degradation products of cellulose, derivatives of sugars (e.g., methyl pentoses), and mixtures of hexosans (e.g., gluco-xylan and arabano-galactan).

The celluloses include both the hexosans, such as mannan, galactan, and glucosan, and the pentosans, such as xylan and araban. Part of these celluloses are strongly associated with the cellulose in wood and are not readily removed by alkali. The exact nature of this association is highly controversial, and various theories have been suggested, among which are: (1) the mixed chain theory, which assumes that a small number of pentose units are incorporated in the cellulose molecule; (2) the mixed crystallization theory, which assumes that some celluloses exist in the cellulose crystallites; (3) the chemical combination theory, which assumes the existence of ester or ether linkage between the celluloses and cellulose chains; (4) the structural theory, which holds that the configuration of the building units in the outer layer of the secondary wall prevents access to the celluloses.

The polyuronides are amorphous substances which contain large amounts of hexuronic acids, some methoxyl and acetyl groups, and some free carboxylic acid groups, although many of these latter groups may be involved in anhydride or lactone formation. The polyuronides are mainly associated with the lignin, although some association exists with the cellulose.¹⁵⁴ The strong association between the polyuronides and the lignin is manifested by the fact that it is impossible to remove all the lignin from wood without losing a considerable part of the hemicellulosic material. Once wood has been delignified, the polyuronides become more readily soluble in dilute alkali.

The total hemicellulose content of wood varies from about 15 to 18% (in softwoods) to about 22 to 34% (in hardwoods). Of a total hemicellulose content of 34%, Ritter¹⁵⁵ reports that about 22% are associated with

¹⁵¹ H. E. Obermanns, *Paper Trade J.* 103, No. 7: 109-117 (Aug. 13, 1936)

¹⁵² B. B. Thomas, *Paper Ind.* 27, No. 3: 374-378, 382 (June, 1945)

¹⁵³ L. F. Hawley and A. G. Norman, *Ind. Eng. Chem.* 24, No. 10: 1190-1194 (Oct., 1932)

¹⁵⁴ E. Schmidt, cited in *Natural and Synthetic High Polymers*, by K. H. Meyer. Interscience Publishers, Inc., New York, N. Y. (1942)

¹⁵⁵ G. J. Ritter, *Paper Trade J.* 105, No. 25: 355 (Dec. 16, 1937)

the cellulose and about 12% with the lignin. The hemicelluloses occur with the cellulose in the cell wall layers of the fiber, particularly in the amorphous regions, and also in the middle lamella. If the lignin is removed from a piece of wood by a suitable lignin solvent, the wood still retains its microstructural pattern because of the hemicellulose in the middle lamella which holds the cells together.¹⁵⁶

The hemicellulose content of commercial wood pulps is often quite different from that of the original wood. The part of the hemicelluloses remaining in the pulp after pulping and bleaching play an important role in papermaking, particularly in regard to fiber preparation and fiber bonding.¹⁵⁷⁻¹⁵⁹ (See Chapters VI and VII, "Fiber Preparation" and "Nature of Fiber Bonding.")

¹⁵⁶ G. J. Ritter, *Tappi* 32, No. 1: 11-20 (Jan., 1949)

¹⁵⁷ R. Vincent, *Paper Trade J.* 113, No. 15: 200-202 (Oct. 9, 1941)

¹⁵⁸ L. E. Wise, *Paper Ind.* 27, No. 6: 825-829 (Sept., 1947)

¹⁵⁹ R. Vincent, *Paper Trade J.* 122, No. 4: 31-35 (Jan. 24, 1946)

LIGNIN

Lignin is one of the major substances present in wood, occurring in amounts ranging from about 17 to 32% of the weight of moisture-free wood. Unfortunately, little is known concerning the fundamental chemical and physical properties of lignin. There are several reasons for this. One is the highly complex nature of lignin which, so far, remains a mystery and another is that lignin seemingly varies in wood of different species and also varies according to the age of the wood in the same species.¹ Still a third reason is the difficulty of isolating lignin in an unchanged condition for study. All the physical properties reported in the literature have been determined on isolated lignin or lignin derivatives.

Isolation of Lignin

Lignin is used as a generic term and must be qualified according to the source and the method used for isolation, for example ethanol extracted lignin from spruce. There are two general laboratory methods for the isolation of lignin. The first involves dissolution of the cellulose by means of 72% sulfuric acid, supersaturated hydrochloric acid (42%), or cuprammonium to leave the lignin as an insoluble residue. The second method involves treatment of the wood with lignin solvents such as aqueous or alcoholic sodium hydroxide at high temperatures (170–180° C.) to extract the lignin which is subsequently precipitated from solution with mineral acids.

The Klason method, which is the 72% sulfuric acid method, involves the treatment of 1 g. of 60-mesh wood meal with 20 ml. of 72% sulfuric acid at 25° C. for about 2 hours, after which the solution is diluted to 3%, digested, and the lignin is collected on a filtering crucible, washed, and dried. The Klason method is unsuited for hardwoods, since these species produce insoluble decomposed carbohydrates by this method. There are two other methods similar to the above in which hydrochloric acid is used. In one method, 1 g. of wood is suspended in 20 ml. of ordinary concentrated hydrochloric acid, saturated with dry acid, and then left from 18 to 20 hours at room temperature. In the other method, supersaturated hydrochloric acid (42%) is used from the start. Although all these methods are used, it

¹ W. M. Fuchs, *Paper Trade J.* 102, No. 13: 181–184 (Mar. 26, 1936)

should be emphasized that none of them will produce an isolated lignin which is the same as that in the original wood.

One of the most important considerations in carrying out the above tests is to use finely ground wood which has been extracted for at least 45 hours with alcohol-benzene to remove the resins and waxes. If these resins are not entirely removed, they will show up in the insoluble lignin residue. The size of the wood is also quite important and should be between 40 and 60 mesh.

One of the newer methods for the isolation of lignin involves the extraction of lignin by means of alcohols such as methanol or butanol in the presence of a small amount of anhydrous hydrogen chloride. This method is interesting because it results in less change in the lignin molecule compared with that obtained by older methods. Dioxane has also been used as a solvent, but it removes only a fraction of the total lignin in the original wood. If hydrochloric acid is used with dioxane, more lignin is removed, but it is changed in structure. Some work has been done on lignin recovered from commercial waste pulping liquors, but this lignin has been drastically changed in structure.

Any of the above methods can be used for determining the amount of lignin in a given sample of wood or pulp. A different method of calculating the lignin content of pulp is by means of the methoxyl content. This method is totally unsuited for calculating lignin in wood, owing to the methoxyl content of other constituents, but it gives fair results on pulps and waste pulping liquors, once the correct factor for the species and pulping conditions has been determined. The following equation has been found suitable for sulfite pulps:²

$$\text{Per cent lignin in pulp} = \frac{\text{Per cent methoxyl content of pulp}}{0.148}$$

However, methoxyl content is not a good indication of lignin content when only a small amount of lignin is present,³ on account of the large error introduced by the methoxyl content of the non-lignin materials. Work by Lange⁴⁻⁶ in Sweden has indicated that the amount of lignin at various points in wood can be determined approximately by ultraviolet absorption readings under the microscope. In this technique, thin wood sections are used so that the intensity of absorption of ultraviolet light of different wavelengths can be measured. This method agrees quite well with the chemical methods.

² M. Baum, J. W. Bard, J. R. Salvesan and G. J. Brabender, *Paper Trade J.* 126, No. 9: 129-133 (Feb. 26, 1948)

³ O. Kress and E. H. Voigtman, *Paper Trade J.* 97, No. 7: 29-44 (Aug. 17, 1933)

⁴ P. W. Lange, *Svensk Papperstidn.* 50, No. 11: B130-134 (1947)

⁵ P. W. Lange, *Svensk Papperstidn.* 47, No. 11: 262-265 (1944)

⁶ P. W. Lange, *Svensk Papperstidn.* 48, No. 10: 241-245 (1945)

Physical Properties of Lignin

Lignin has a density of about 1.3 and a refractive index of about 1.6. Lignin is an amorphous substance, even though it exists in an orderly morphological arrangement in certain parts of the fiber. The amorphous character of lignin makes it difficult to analyze, since x-ray examination and melting point determinations, are not applicable.

Although lignin is not as highly polymerized as cellulose, it definitely belongs to the class of high molecular weight polymers. Native lignin may be regarded as an amorphous resin of varying molecular weight and solubility. The shape of the molecule is unknown, but it definitely does not have the linear form of cellulose. The exact molecular weight is also unknown, but many lignin chemists use a basic building unit of about 840 for making calculations, since this value seems to fit most of the analytical data. The true molecular weight is considered to be a multiple of 840.

Chemical Constitution of Lignin

The percentage composition of lignin has been determined with a fair degree of certainty, and is approximately as follows for coniferous woods:

Carbon	63.5%
Hydrogen	6.0%
Methoxyl	15.0%

In hardwood lignins, the carbon content is somewhat lower.

Considerable work has been done in an effort to discover the structural formula of lignin, but in view of the inconsistencies and incompleteness of the results, it is impossible to write any formula which is generally accepted. This does not mean that nothing whatsoever is known regarding the lignin formula, because actually considerable information has been amassed regarding the structure of the lignin building unit, its side chains, and its reactive groups.

Most lignin chemists believe that the lignin molecule contains an aromatic nucleus.⁷ Some, however, are of the opinion that the lignin molecule does not contain an aromatic nucleus but rather a nucleus which is readily converted into an aromatic compound.

The existence of a benzene nucleus in lignin is indicated by the fact that aromatic compounds are obtained by either alkaline degradation or oxidation. For example, up to 8% vanillin is obtained on the alkaline



Fig. II-1. Vanillin.

⁷ P. W. Lange, *Svensk Papperstidn.* 48, No. 10: 241-245 (1945)

hydrolysis of lignosulfonic acids, and up to at least 20% vanillin is obtained upon the oxidation of isolated lignins in coniferous woods with alkaline nitrobenzene. The formula of vanillin is given in Figure II-1. The presence of a benzene nucleus is further proved by the research on the hydrogenation of lignin by Harris and coworkers,⁸ who obtained 1-propyl-4-cyclohexanol, 1-propyl-3,4-cyclohexanediol, and 3-(4-hydroxycyclohexyl)-1-propanol in a yield of about 50% of the lignin used.

According to Freudenberg and, more recently, Hibbert and his coworkers, the lignin molecule is composed of phenylpropane lignin building stones. Klason proposed as early as 1896 that spruce lignin is closely related to coniferyl alcohol. The fundamental nature of the building units is indicated by the fact that it is possible to isolate fission products from lignin containing ten carbon atoms in the form of an aromatic ring connected with

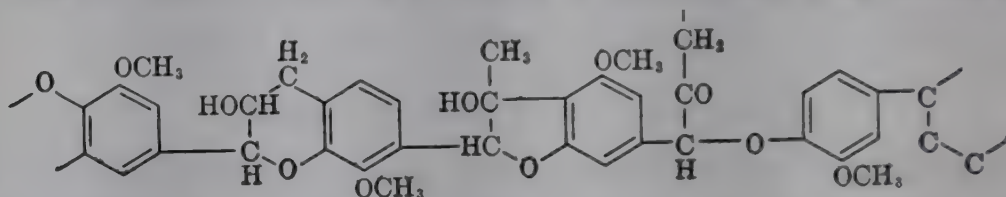


Fig. II-2. A scheme of a lignin molecule according to Freudenberg.

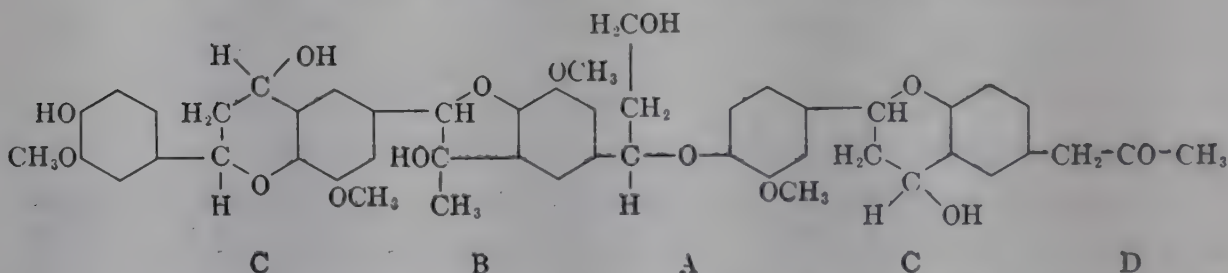


Fig. II-3. A scheme of a lignin molecule according to Brauns (courtesy Dr. F. E. Brauns, Institute of Paper Chemistry).

a straight chain of three carbon atoms.^{8a} The lignin molecule consists of a large number of these building units which are linked together through the side chains to form a high molecular weight polymer. A scheme proposed by Freudenberg to show how these building units are linked together is given in Figure II-2. A somewhat different scheme, proposed by Brauns to reconcile other theories with those of Freudenberg, is shown in Figure II-3.

Lignin contains a number of reactive groups. Each of the basic building units of 840 is composed of five phenylpropane building stones and contains four hydroxyl groups (three aliphatic and one phenolic), four methoxyl groups, and one carbonyl group. The reactivity of lignin is controlled principally by the hydroxyl groups. All the hydroxyl groups can be acetylated or alkylated and, in addition, the phenolic hydroxyl group can react

⁸ E. E. Harris, J. D'Janni and H. Adkins, *J. Am. Chem. Soc.* 60: 1467 (1938)

^{8a} H. Hibbert, *J. Am. Chem. Soc.* 61, 725-731 (Mar., 1939)

with alkali. According to Freudenberg, primary hydroxyl groups are absent, and only secondary or tertiary hydroxyls are present. Erdtman^{9, 10} postulates two different hydroxyl groups, one which reacts with bisulfite at pH 6 to 8 and with phenols at pH 1 to 2, and another which reacts with bisulfite only at pH 0 to 2 and not with phenols. It is generally believed that there are no carboxyl groups in the lignin molecule.

The presence of methoxyl groups (OCH_3) is definitely established, but the methoxyl content of lignin varies, depending upon its source. Klason was the first to suggest that there is one methoxyl group for each ten carbon atoms in lignosulfonic acid obtained from waste sulfite (spruce) cooking liquor. The methoxyl content is believed to be between 14 and 15% of the lignin in spruce (four methoxyls per building unit) and 20 to 21% methoxyl for hardwoods (six methoxyls per building unit). The higher methoxyl content of hardwood lignin is due to the syringyl groups.

Differences in Hardwood and Softwood Lignins

As already pointed out, lignin is not a definite compound but rather a collection of similar compounds which have the same general structure but different molecular weights. Hardwood lignin differs appreciably from softwood lignin. In the former, the building unit appears to be phenolic nuclei of both propyl guaiacyl and propyl syringyl, whereas in softwood lignin, the building unit appears to be almost entirely of the propyl guaiacyl type. As a result of this difference, hardwood and softwood lignosulfonic acids produce different end products under alkaline hydrolysis (e.g., a spent liquor from softwoods yields compounds with a vanillyl grouping, whereas a spent liquor from hardwoods yields compounds with a syringyl grouping, as well as those with a vanillyl grouping). For this reason, only a pulping spent liquor from coniferous woods can be used for the commercial production of vanillin.

A quick method for differentiating between hardwood and softwood lignins is the so-called Mäule test. In this test, the lignified material is treated with 1% potassium permanganate solution for a few minutes at room temperature and washed; then, the brown-colored material is treated with 12% hydrochloric acid, washed again, and moistened with ammonium hydroxide. Oak, maple, beech and other hardwood species produce a deep purple-red color, whereas spruce and other softwood species produce a pale brown or yellow color.

Location of Lignin

It is well known that lignin is not distributed uniformly throughout

⁹ H. Erdtman, *Tappi* 32, No. 2: 71-74 (Feb., 1949)

¹⁰ H. Erdtman, Talk given at Wood Chemistry Meeting, Lignin Round Table, Appleton, Wis. (Aug. 12-14, 1948)

the wood. As early as 1925, Ritter¹¹ demonstrated microscopically that the lignin in wood is located chiefly in the middle lamella and primary wall of the fiber, i.e., in the "compound middle lamella." More recently, Carpenter and Lewis¹² showed very positively that there is a lignin sheath surrounding softwood fibers. The distribution of lignin in the middle lamella and primary and secondary walls of the fiber has already been discussed in the preceding chapter. As pointed out there, the "compound middle lamella" has been shown to contain 71% lignin.¹³

A number of factors influence the lignin content of wood. For example, the lignin content is higher (and the cellulose content correspondingly lower) in the sapwood than it is in the heartwood. Springwood fibers contain a higher percentage of lignin than the summerwood fibers, because they have a greater proportion of middle lamella. Wood ray cells are higher in lignin than the wood fibers or tracheids.

Since lignin is removed preferentially from different parts of the fibers during cooking of the wood, the distribution of lignin in cooked pulps is rarely the same as it was in the original wood. Most of the lignin exists in the outer walls of the fiber when the lignin content is over 8%,¹⁴ but under some conditions of pulping, the lignin may be present in greatest amount in the inner or secondary wall of the fiber when the lignin content is less than 8%.

The Lignin-Carbohydrate Bond

It is generally believed that most of the lignin in wood is combined with other components, but the exact manner in which the lignin is bound has been a controversial subject for many years. Among the possibilities which have been suggested are: a physical mixture of lignin and cellulose, an adsorption of lignin by cellulose, and a chemical combination of the lignin with the carbohydrates in the fiber. Although there has been considerable discussion of these various theories, there is very little agreement among chemists.

As early as 1903, Cross and Bevan suggested that lignin was chemically combined with cellulose in woody plants in the form of a substance which they termed "lignocellulose." Today, most chemists believe that a true chemical bond exists between the lignin and part of the hemicellulose fraction, i.e., the polyuronides, but that only part of the lignin is combined in this way, and that the remainder of the lignin is held in some weaker association. Ritter¹⁵ and Harlow¹⁶ demonstrated that there are two principal

¹¹ G. J. Ritter, *Ind. Eng. Chem.* 17, No. 11: 1194-1197 (Nov., 1925)

¹² C. Carpenter and H. F. Lewis, *Paper Trade J.* 99, No. 3: 37-42 (July 19, 1934)

¹³ H. J. Bailey, *Ind. Eng. Chem., Anal. Ed.* 8, No. 5: 389-391 (Sept., 1936)

¹⁴ H. F. Lewis, F. E. Brauns and M. A. Buchanan, *Paper Trade J.* 110, No. 5: 58-60 (Feb. 1, 1939)

¹⁵ G. J. Ritter, *Ind. Eng. Chem.* 20, No. 9: 941-945 (Sept., 1928)

¹⁶ W. M. Harlow, *Tech. Pub. No. 24*, New York State College of Forestry, Syracuse, N. Y. (1928)

ways in which lignin exists in the fiber, as middle lamella lignin and as cell wall lignin. Recent evidence indicates that the lignin in the secondary wall is oriented, but that the lignin in the primary wall is not. Methylation experiments have indicated that certain of the hydroxyl groups in the lignin molecule are "covered" and cannot be freed without hydrolysis.¹⁷ These groups are probably involved in a lignin-carbohydrate bond.

Jayme¹⁸ pointed out that about 97% of the lignin can be removed without fiber damage, but that the remaining 3% cannot be removed without destroying the fiber, thereby indicating that a small part of the lignin is chemically combined, or that it penetrates the fiber so deeply that the fiber structure is destroyed when it is removed. Likewise, the sudden increase in pentosan loss which occurs during the removal of the last part of the lignin with chlorine dioxide indicates that this part of the lignin is in very intimate association or chemical combination with part of the pentosans.¹⁹ For example, Jahn and Holmberg²⁰ found, in the delignification of aspen (60 to 100 mesh) with chlorine dioxide, that the pentosan loss increased from 2.8 to 11.2% when the lignin was reduced from 4.78 to 0.17% (original lignin content 17.26%). In the same manner, chlorination of pulp (which is considered specific for lignin) renders part of the hemicellulose in the pulp more easily removed.

Several different types of bonds between the lignin and the carbohydrates in the fiber have been proposed, and it is likely that more than one type is present. Among the types of bond which have been suggested are the acetal linkage, ether-type linkage, and the glucosidic linkage. Hibbert²¹ postulated the presence of a stable linkage, possibly of an ether type. Other investigators favor a phenol-ether type linkage which is formed between the phenolic hydroxyl groups of the lignin molecule and the hydroxyl groups in the polyuronide fraction of the hemicelluloses, but most of the evidence points to the fact that the phenolic hydroxyl groups in lignin are free and not chemically combined. An ester type linkage between the lignin and uronic acids is also unlikely because this type of linkage is very easily hydrolyzed. Brauns and Yirak²² list seven possible variations of the acetal or half-acetal hydrolyzed linkage which may occur at the carbonyl group of the lignin molecule. It is possible that part of the lignin is strongly bound to hemicellulose by means of an ether type linkage, and another part only weakly held by an acetal linkage.

¹⁷ E. E. Harris, E. C. Sherrard and R. L. Mitchell, *J. Am. Chem. Soc.* 56: 889 (1934)

¹⁸ G. Jayme, *Cellulosechemie* 20, No. 2: 43-49 (Mar., Apr., 1942)

¹⁹ C. V. Holmberg and E. C. Jahn, *Paper Trade J.* 111, No. 1: 1-4 (July 4, 1940)

²⁰ C. V. Holmberg and E. C. Jahn, *Paper Trade J.* 111, No. 1: 1-4 (July 4, 1940)

²¹ H. Hibbert, *Paper Trade J.* 113, No. 4: 39-48 (July 24, 1941)

²² F. E. Brauns and J. J. Yirak, *Paper Trade J.* 125, No. 12: 135-140 (Sept. 18, 1947)

Reactions of Lignin

Lignin is a highly reactive substance. As mentioned above, its molecule contains hydroxyl groups (both phenolic and aliphatic), carbonyl groups, and methoxyl groups. Most of these different groups are free to undergo their characteristic reactions.

The hydroxyl groups in the lignin molecule can be readily acetylated or alkylated. Methylation can be carried out with dimethyl sulfate. Thus, by means of methylation, Heuser and coworkers²³ were able to increase the methoxyl content of lignin from its original value of 14.6% to nearly 26.3%. Brauns²⁴ was able to obtain a product with 32.3% methoxyl by more complete methylation. In the case of spruce wood meals, Brauns and Yirak²⁵ increased the methoxyl content from 4.7 to 38.1%, but all of this was not due to methylation of the lignin alone. They believe that the fact that soluble isolated lignin and insoluble hydrochloric acid lignin can both be methylated to the same value is an indication that the lignin molecule is polymerized through some other means than by condensation through hydroxyl groups. An acetyl content of 22.5% is obtained on complete acetylation of lignin.

Other reactions which lignin will undergo are neutralization, oxidation, reduction, halogenation, nitration, hydrogenation, hydrolysis, and sulfonation. It is generally believed that lignin in freshly cut wood undergoes condensation and polymerization, and that these reactions are accelerated by the presence of traces of acids and increased temperatures.²⁶ This partly explains why old wood is somewhat more difficult to pulp (by the sulfite process) than wood which is freshly cut.

Of all the reactions which lignin undergoes, sulfonation, oxidation, and halogenation are of particular importance to the pulp and paper chemist because of their relationship to the pulping and bleaching processes. In sulfite pulping, a water-dispersible lignosulfonic acid is produced. In the soda process, alkali-soluble alkali lignin is produced. In the sulfate process, sulfur enters the lignin molecule to form alkali-soluble thioglignin. If wood is cooked with nitric acid, part of the lignin is converted into water-soluble products and part is nitrated. If the process is not carried too far, an alkali-soluble "nitro lignin" is produced.

Lignin is very susceptible to oxidation, and even under mild oxidizing conditions, it is broken down into aromatic acids like benzoic and protocatechuic. Under more drastic conditions, lignin is oxidized to acids

²³ E. Heuser, R. Schmitt and L. Gunkel, *Cellulosechemie* 2: 81-86 (1921) through *C. A.* 16, No. 3: 490 (Feb. 10, 1922)

²⁴ F. E. Brauns, *J. Am. Chem. Soc.* 61, No. 8: 2120-2127 (Aug., 1939)

²⁵ F. E. Brauns and J. J. Yirak, *Paper Trade J.* 125, No. 12: 135-140 (Sept. 18, 1947)

²⁶ F. E. Brauns, *Tappi* 32, No. 4: 157-160 (Apr., 1949)

such as formic, acetic, oxalic, and succinic. Under the relatively mild conditions which prevail in commercial bleaching processes, lignin is converted into products which are soluble in either water or alkali. In hypochlorite bleaching, water-dispersible products are produced by reactions in which the phenolic hydroxyl group in the lignin molecule appears to play a prominent role.²⁷ In the chlorination process, where straight chlorine is used, both substitution and additions of chlorine in the lignin molecule take place. Lignin is very readily chlorinated, and it is possible to obtain chlorinated products containing up to 25 to 38% chlorine when isolated lignin is used, although this high degree of chlorination is not obtained in commercial bleaching. These chlorinated lignins are soluble in alkali and have a lower methoxyl content than the original lignin.²⁸ If chlorination is carried beyond about 35%, appreciable degradation of the lignin is obtained. The reactions which occur in the various commercial pulping and bleaching processes are discussed in greater detail in the chapters on pulping and bleaching.

Miscellaneous Properties of Lignin

Isolated lignin has an acid character and carries a negative electrostatic charge, as indicated by its tendency to adsorb basic dyestuffs. This property of lignin, which is probably due to acidic phenolic hydroxyl groups present in the lignin molecule, contributes to the acidity and negative character of pulp fibers.²⁹ Lignin has a pronounced effect on the dyeing, ion exchange, adsorption, and other properties of pulp fibers. The lignin in unbleached sulfite pulp, which contains sulfonic acid groups, has definite ion exchange properties. According to Lautsch,³⁰ a cation-binding value up to 2 gram equivalents per kilo of dry isolated lignin resin is obtainable.

It is known that native lignin and lignins which have been isolated with the aid of organic agents are thermoplastic and will flow if subjected to heat and pressure. In the Masonite process (see chapter on pulping), the thermoplastic property of lignin is utilized so that the lignin acts as a binder in the pressed wood. Because of its similarity to phenol, isolated lignin obtained from waste cooking liquor is sometimes sold as a filler for use in phenol formaldehyde molding compounds. However, lignin has a low ratio of phenolic groups, having only one phenolic group per building unit of 840, so that it offers little opportunity for cross linkages to take place during molding. The various uses of commercial lignins obtained as by-products from the pulping of wood are described in the chapter on pulping.

²⁷ F. E. Brauns, *Paper Trade J.* 103, No. 5: 72-75 (July 30, 1936)

²⁸ E. E. Harris, E. C. Sherrard and R. L. Mitchell, *J. Am. Chem. Soc.* 56, No. 4: 889-893 (Apr., 1934)

²⁹ C. M. Sigvardt, *Paper-Maker* 110, No. 6: TS55-61 (Dec., 1945)

³⁰ W. Lautsch, *Die Chemie* 57: 149-154 (1944) through *C. A.* 40: 5915 (1946)

PULPWOOD

Wood is the most important raw material of the pulp and paper industry. It constitutes over 90% of the fibrous raw material used in the manufacture of papermaking pulp in the United States. At least one-third of the cost of making pulp can be attributed to the cost of wood. It is, therefore, logical that the pulp chemist should give considerable attention to the evaluation of pulpwood.

A complete evaluation of pulpwood, for use in commercial operations or for laboratory study, includes the determination of a large number of facts concerning the species, history, and characteristics of the wood. For routine commercial work, it is usually necessary to determine only a small part of the data which is required for laboratory research purposes. Some of the general characteristics of pulpwood which should be considered in evaluation studies are discussed in the following sections under the headings: (1) Species of Wood, (2) Physical Characteristics of the Cord, (3) Anatomy of Wood, (4) Physical Properties of Wood, (5) Minor Chemical Components of Wood, and (6) History of Wood.

Before starting an evaluation of wood, it is necessary to obtain a representative sample, since wood is, by nature, extremely variable. Sampling of pulpwood presents a difficult problem, owing to the bulk and weight of the material being handled and its relative non-uniformity. In the case of pulpwood, commercial sampling is best done while the material is being moved, as on a conveyor, the sample being taken by removing logs from the conveyor at regular intervals, such as taking every fiftieth log, until an adequate sample is obtained. If the wood is being handled by a crane, several crane loads, taken at random, should provide a satisfactory sample. Shipments of pulpwood for laboratory use are generally small, and if they consist of one cord or less, the entire lot should be taken for the sample. If the shipment consists of more than one cord, every second or every third log should be selected, until a full cord is obtained for the sample. The adequacy of a sample depends upon the degree of variability of the characteristic under examination and the precision required in the results. The physical characteristics and properties of pulpwood vary between wide limits, and it is highly desirable to take a sample which is large enough to give reasonable precision.

Species of Wood

There are two principal classes of wood: (1) gymnosperms or evergreens, commonly called softwoods, and (2) angiosperms or deciduous trees, commonly called hardwoods. The approximate general properties of these two classes of wood are given in Table I.

TABLE I
COMPARISON OF HARDWOODS AND SOFTWOODS

	Softwoods	Hardwoods
Major type of fiber	Tracheids	Wood fibers and vessels
Length of fibers	2.5 to 3.0 mm. for eastern species 3.5 to 5.0 mm. for southern and western species	Wood fibers 0.6 to 2.0 mm. Vessels shorter and very wide
Lignin, %	25-32	17-26
Cellulose (Cross and Bevan), %	55-61	58-64
Pentosan content, %	8-13	18-25
Density of green wood (lb./cu. ft.)	21-26	22-35

Softwoods are considered to be more desirable for pulp and papermaking than hardwoods. However, the growing scarcity of good pulpwood has made it necessary to use hardwoods in greater quantity, and the pulp and paper industry has learned that it can utilize hardwoods to good advantage in certain processes. Some mills use a certain percentage of hardwoods mixed with softwoods, but, in general, the two classes of wood should be pulped separately for best results.

Softwoods are more homogeneous than hardwoods. They contain principally fibers or tracheids, whereas hardwoods contain several main elements (fibers, tracheids, and vessels). The fiber length of the softwoods is greater than that of the hardwoods, and for this reason, papers made from softwood pulp generally have from 30 to 100% greater strength than papers made from hardwood pulps. Strong pulps can, however, be made from the hardwoods by certain processes.

Hardwoods contain a higher percentage of pentosans and other hemicelluloses (but much less mannan) and have a lower lignin content (particularly in the secondary wall) than softwoods. The density is higher than that of softwoods, which is a disadvantage from the standpoint that it prevents the use of water transportation and increases the power consumption in the chipping of the wood prior to pulping. However, the high density, high cellulose content, and low lignin content of hardwoods are highly beneficial in increasing the yield of pulp per cord of wood, as well as per unit

TABLE II
DENSITY AND CHEMICAL COMPOSITION OF SOME EASTERN AND LAKE STATES SPECIES*

Species	Density (moisture-free weight and green volume) lb./cu.ft.	Chemical composition of wood (moisture free), %											
		Holocellulose				Cross and Bevan cellulose		Lignin	Total pentosans	Solubility in		Ash	
		Total		Alpha	Total	Alpha	Ether			1% caustic soda	Hot water		
		Total	Alpha										
Hardwoods													
Quaking aspen (<i>Populus tremuloides</i>)	22	82	51	64	48	17	23	1.0	19	3	0.3		
American beech (<i>Fagus grandifolia</i>)	34	78	..	61	47	23	20	0.8	21	2	0.2		
Paper birch (<i>Betula papyrifera</i>)	34	60	41	25	26	1.5	19	4	..		
Yellow birch (<i>B. lutea</i>)	34	61	25	0.6	20	4	0.5		
Eastern cottonwood (<i>Populus deltoides</i>)	23	63	46	24	19	0.3	15	2	..		
Sugar maple (<i>Acer saccharophorum</i>)	35	76	..	57	42	23	21	0.3	20	3	0.2		
Silver maple (<i>A. saccharinum</i>)	32	83	..	61	47	21	18	0.7	15	2	0.2		
Yellow poplar (<i>Liriodendrum tulipifera</i>)	25	62	45	20	19	0.2	17	2	..		
Black cherry (<i>Prunus serotina</i>)	30	85	..	60	45	21	20	0.9	18	4	0.1		
White oak (<i>Quercus alba</i>)	37	51	..	32	22	0.7	23	5	0.4		
Softwoods													
Balsam fir (<i>Abies balsamea</i>)	21	70	44	58	42	29	11	1	11	4	0.5		
Eastern hemlock (<i>Tsuga canadensis</i>)	24	68	48	56	43	32	10	0.7	13	4	0.4		
Jack pine (<i>Pinus banksiana</i>)	24	72	49	58	41	27	13	2	13	4	..		
Eastern white pine (<i>P. strobus</i>)	21	60	44	28	11	5	16	5	..		
Red pine (<i>P. resinosa</i>)	27	54	..	24	11	5		
Black spruce (<i>Picea mariana</i>)	24	61	44	27	11	1	11	3	0.3		
Red spruce (<i>P. rubra</i>)	24	73	48	60	43	27	12	1.5	0.2		
White spruce (<i>P. glauca</i>)	24	73	49	61	44	27	11	1.5	12	3	0.3		
Tamarack (<i>Larix laricina</i>)	31		

* Typical values obtained at Forest Products Laboratory; wide variations may occur within single species.

weight of wood. Even those hardwoods which are low in density (e.g., aspen) produce higher yields per cord than softwoods because of their high cellulose content. Hardwoods are generally more difficult to bark than softwoods, except during certain seasons of the year.

Differences between species of wood are generally less marked than differences between the two main classes of softwoods and hardwoods. There are, however, notable differences among species, and these differences are often sufficiently great to affect very markedly the pulping, bleaching, and general papermaking qualities of the pulp.

In the eastern and midwestern part of the United States, the most desirable softwood species are white, red, and black spruce, eastern hemlock, and balsam fir. Spruce is the most desirable species, but eastern hemlock also makes good pulp. Balsam is likely to produce pulps in low yield. Jack pine produces pulp of fair quality except that the amount of screenings is likely to be high. The principal hardwoods used are aspen, birch, beech, and some maple. Typical analyses of eastern and lake states hardwood and softwood species are given in Table II.¹

In the western states, western hemlock, sitka spruce, and the true firs are the desirable species. Western hemlock produces an excellent pulp of high strength which can be bleached without difficulty. Sitka spruce has the largest fiber size of the common western woods, but so far, it is not widely used. Sitka spruce is slightly superior to hemlock and true firs and is highly prized because of its good color. Western red cedar produces pulps of better strength (except tearing strength) than most other western species, but it has a high extractive and high lignin content, and the pulp has a high bleach requirement. Most of the western woods are low in pentosan content, being only about 7 to 9%, compared with 12 to 14% for the eastern and southern softwood species.

In the southern states, the important species are the pines, e.g., short-leaf (*P. echinate*), loblolly (*P. taeda*), slash (*P. caribaea*), and longleaf (*P. palustris*). Hardwoods, e.g., gums and oak, are sometimes used by southern mills. Many other species than those mentioned above can be used for pulping, and in recent years there has been a definite broadening in the number of species used.

Classification of wood by species is done by inspection of the wood and the bark in accordance with the procedures of the wood technologist.² Regardless of the claims of the shipper, it is advisable to check all wood shipments for identification to be sure that they are as represented. It is often stipulated by the buyer that shipments shall contain not more than a speci-

¹ "Pulpwood," *TAPPI Monograph No. 4*, 130-152. Tech. Assoc. Pulp & Paper Ind., New York, N. Y. (1947)

² See TAPPI Standards

fied percentage of certain species, and in order to check on this, it is necessary to identify individually a large number of sticks from the shipment to make sure that the stipulated amount is not exceeded. For laboratory purposes, of course, it is essential that every stick used be positively identified as the type desired.

Physical Characteristics of the Cord

Wood is commonly bought and sold on the basis of gross volume. The most common unit of measure is the cord, the volume occupied by bolts of wood 4 ft. long when stacked in a pile $4 \times 4 \times 8$ (128 cu.ft.). In the southern states a unit based upon 5-ft. lengths is frequently used (160 cu.ft.). A basis of measure growing in use is the cunit, the quantity of unbarked wood containing 100 cu.ft. of solid wood. It is roughly equal to the cord.

It is frequently desirable to determine the amount of solid wood contained in a cord. The dry weight of wood in a cord can be determined (1) by measurement of the volume and density of the wood in the cord or (2) by determining the wet weight and moisture content of the wood in the cord.

One of the most widely used methods of measuring the cord is by density and volume measurements taken on a sample cord. About 0.1% of the total shipment of wood is selected in such a manner as to be truly representative of the entire cost, and then this wood is carefully racked in a cord rack ($8 \times 4 \times 4$ ft.) and selected logs removed for measurement. The logs are selected along the two diagonals of the cord to furnish about 20% of the total logs in the cord for testing.³

After selection of the sample logs, two disks are cut from each of the test logs, and each disk is tested for weight, diameter, weight of peeled disk, diameter of peeled disk, weight of disk immersed in water, weight of disk saturated with water, diameter of saturated disk, and weight of oven-dry disk. The following values are then obtained from these data: (1) average diameter of log, (2) maximum and minimum diameters of log, (3) percentage of bark, by volume and by weight, (4) percentage moisture, (5) specific gravity, and (6) density, of green and dry wood. The following calculations are then made: (1) number of logs in the sample cord, (2) total weight of logs in the cord, (3) average length of logs in the cord, (4) percentage excess length, (5) volume of peeled wood in cubic feet, (6) total volume per cord $[(\text{peeled volume} \times 100) \div (100 - \text{per cent bark by volume})]$, (7) oven-dry wood per cord (volume peeled wood \times density based on moisture-free wood and green volume).

In the case of wood which is shipped to the mill by rail, it is desirable to check the relationship which holds between the sample cord and the measured cord in the shipment. In order to obtain this information, one or two

³ See TAPPI Standards

cars of wood are selected at random and are carefully measured to determine the number of cords of wood contained in the car. The wood from the measured car is unloaded separately from the remainder of the shipment and is carefully racked in the sample cord rack, alternately filling and emptying the rack. From the data thus obtained, a factor which will relate the scaled cord to the laboratory cord may be calculated and used to correct results obtained from the laboratory cord to a basis comparable with the commercial scaled cord. In some cases, direct determination of the cord scaled on a railroad car can be made by sampling the cars of wood at random.

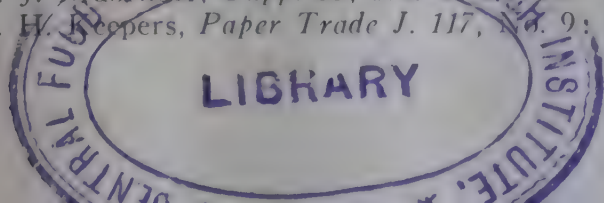
Another method of measuring the amount of solid wood volume is by water-displacement, a very accurate method, although one which is considered by many to be too time-consuming and costly for regular production. However, in some mills,⁴ every cord of wood used in the mill is measured by loading the wood into cages and submerging them in large tanks of water where the rise in water level indicates the volume of water equivalent to the volume of wood in the cage. Another method for determining the solid volume of wood in a stacked cord is the photographic method by which the stacked wood is photographed and the area of wood determined with the aid of a planimeter.⁵

The amount of solid wood per cord is influenced by the compactness of the pile, density of the wood, amount of defective wood, amount of bark, diameter of the logs, length of the logs, and degree of straightness of the logs. Increasing the average diameter of the logs increases the solid-wood content of the cord,^{6,7} although Brabender⁸ has pointed out that this is true only with selected logs and not with woods-run timber. The effect of length of logs on the amount of solid wood per cord is shown in Table III for spruce bolts, carefully selected and stacked.⁹ The more pronounced degree of crook in the longer bolts accounts for the lower volume of wood and fewer sticks per cord.

TABLE III

EFFECT OF BOLT LENGTH ON AMOUNT OF SOLID WOOD IN A CORD OF PEELED SPRUCE

	Length of bolts		
	8 ft.	4 ft.	2 ft.
Number of sticks per cord	58	122	262
Volume of solid wood per cord, cu.ft.	94.7	98.0	103.4

⁴ J. B. Jones, *Tappi* 32, No. 2: 58-62 (Feb., 1949)⁵ C. H. Keepers, *Paper Trade J.* 117, No. 9: 93-97 (Aug. 26, 1943)⁶ C. H. Keepers, *Paper Trade J.* 117, No. 9: 93-97 (Aug. 26, 1943)⁷ W. Shymanski, *Paper Mill* 58, No. 30: 9-17 (July 27, 1935)⁸ G. J. Brabender, *Tappi* 32, No. 8: 337-339 (Aug., 1949)⁹ C. H. Keepers, *Paper Trade J.* 117, No. 9: 93-97 (Aug. 26, 1943)

Some mills are able to purchase barked wood, but most mills are forced to buy their wood in the unbarked condition. Bark generally amounts to about 15% by volume and 7 to 8% by weight of the dry wood in the cord. Bark is practically useless from a papermaking standpoint, and in most cases, must be removed in special barking apparatus. The loosened bark is considered as waste and is generally disposed of by burning after pressing and drying to remove excess moisture. Bark contains some bast fibers, together with cork cells, and in special cases, it can be mixed with other fiber to produce a coarse grade of building board. Wood room waste consisting of bark and some wood has been used in making a coarse wrapping paper.¹⁰ Redwood bark was used in a small way during World War II in the production of long-life battery separators. The bark of certain species contains a considerable amount of tannin which can be profitably extracted.

Anatomy of Wood

Wood is a cellular, porous material, the cells of which show a great diversity in size and shape. A knowledge of the cellular structure of wood is of value to the pulp chemist, since the anatomical structure of wood has an important influence on the penetration of liquids in pulping and affects the course of the pulping reactions. Wood remains intact during the pulping process, and consequently the pulping chemicals and the by-products of pulping must pass through the pores of the wood.

In softwoods, the principal cell or fiber elements are the tracheids, which are highly elongated, lignified cells with tapering ends having an average length of about 3 to 5 mm. and an average diameter of 0.03 mm. Hardwoods are more complex than softwoods and contain two principal cell types, wood fibers and vessel elements. The wood fibers, which are the predominating cell type, are elongated, thick-walled fibers having an average length slightly over 1 mm. and an average diameter of about 0.02 mm. The vessels are relatively short in length, but have a large diameter. In some hardwoods, the vessels are very large and exist as a definite band in the springwood (ring-porous woods), whereas in other hardwoods, the vessels are nearly uniform in size and are uniformly distributed within the annual ring (diffuse-porous woods). The wood fibers, vessels, and tracheids are aligned longitudinally in the wood, but in all species, there are fine lines of cells extending radially in the wood known as the wood rays. There are also small, thin-walled parenchyma cells which are used principally for the storage of food.

Pits are present in the walls of the fibers and may be simple or bordered, (see Figure III-1). Pits generally exist in pairs between two adja-

¹⁰ A. D. Hamilton, *Pulp Paper Mag. Canada* 51, No. 3: 205-210, Convention Issue (1950)

cent cells in the wood where the pits facilitate the interchange of soluble materials between the cells. The type of pits depends upon whether the pit leads from one tracheid to another or from a tracheid to a longitudinal ray cell. The total number of pits in a given fiber varies, depending upon the type of fiber, and may run up to 150 to 200 for some softwood tracheids.

The principal cell types are described in Table IV. All the cell types present in wood are not listed, as, for example, longitudinal parenchyma cells, which are often present in both hardwoods and softwoods. The volume of the wood occupied by each cell type is given, but it should be pointed

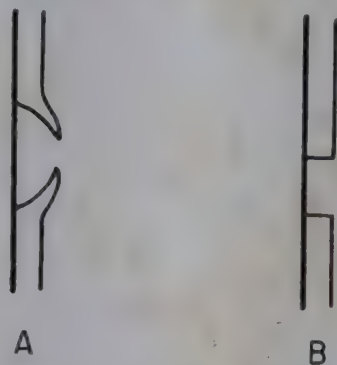


Fig. III-1. Schematic drawing of bordered pit (A) and simple pit (B).

out that the ratio of cell type to the total wood volume is not the same as the ratio of cell type to other cells obtained in the final pulp, since some of the smaller elements are lost in the pulping and screening process.

TABLE IV

PRINCIPAL CELL TYPES FOUND IN WOOD

SOFTWOODS

Tracheids	Tracheids constitute over 90% of the volume of most softwoods. They average about 3 to 5 mm. in length and have tapering ends and numerous bordered pits. Pits are most abundant in the radial walls and toward the ends of springwood tracheids. As a rule, the springwood tracheids have thinner walls and larger diameter than the summerwood tracheids. In Douglas fir spiral thickening occurs on the inside surface of the tracheid walls.
Ray cells	Softwoods contain a small amount (usually less than 10% by weight) of ray cells. These may be ray parenchyma or ray tracheids. All ray cells are narrow and compared to the tracheids are short, being less than 0.2 mm. in length. The ray tracheids have bordered pits, whereas the ray parenchyma contain only simple pits. As a rule, the ray cells are screened out of chemical pulps, but are present in mechanical pulps.
Epithelial cells	In pine, spruce, Douglas fir, and larch, epithelial cells are present surrounding intercellular spaces known as resin canals. These canals may be either transverse or longitudinal, the latter being most important. They have a size up to 0.3 mm. in diameter and contain large quantities of resin. As a rule, the resin canals are disintegrated during pulping.

HARDWOODS

Hardwood fibers	These are three types of hardwood fibers, tracheid, fiber-tracheid, and libriform fiber, the latter being the main fiber. A typical fiber is a long, relatively narrow, empty cell which has thick to thin walls. The tracheids may have bordered pits, but the other fibers may have very fine, elongated pits. Wood fibers average about 1 mm. or slightly more in length. They normally account for 25 to 35% of the volumetric composition of hardwoods and a much greater proportion of the fiber number.
Vessel elements	These are large, empty cells which are found in porous hardwoods. They are from 0.1 to 1.0 mm. in length and vary considerably in shape. They are much wider in diameter, and usually have thinner walls than the wood fibers. The ends of the cells are perforated and, in some cases, contain bars in the form of a grating across the opening. Spiral thickening occurs in the vessels of certain species. In some species, vessels may account for up to 50 to 60% of the volumetric composition of the wood but generally less than 10% by weight.
Ray cells	These are parenchymatous cells (thin-walled and rectangular in shape) which grow at right angles to the wood fibers. These may occupy from 5 to 35% of the volume of the original wood.

It is frequently desirable to identify the species of wood from which the fibers in a given sample of pulp or paper were obtained. This is a part of pulp and paper testing, rather than wood evaluation, but it is mentioned here, since identification is based upon minute cell characteristics visible under a microscope. In the case of hardwoods, identification is based mostly upon the size and shape of the vessels, some typical examples of which are shown in Figure III-2.¹¹ In the case of softwoods, identification is based mostly upon the differences in size, shape, and number of the pits leading from a tracheid to an adjacent ray cell. Portions of different tracheids depicting typical ray crossings for a number of softwood species

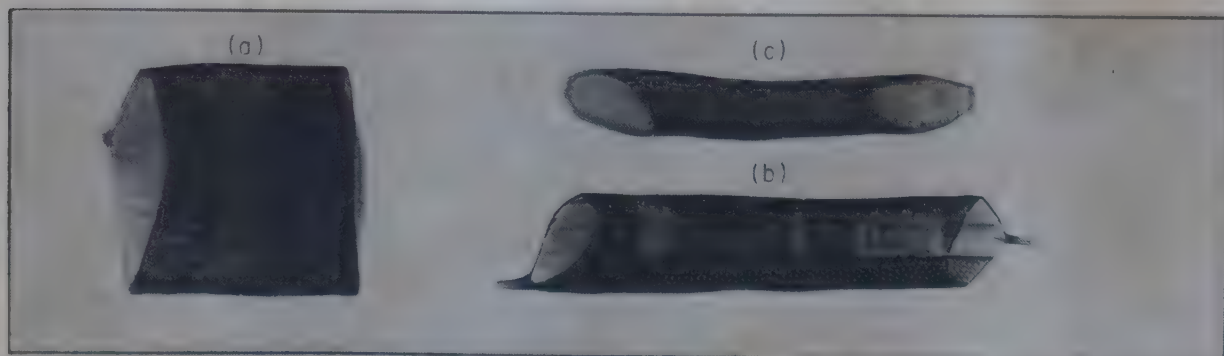


Fig. III-2. Typical vessel segments from several different hardwoods: (a) red oak (*Quercus borealis*); (b) black cottonwood (*Populus trichocarpa*); (c) white birch (*Betula papyrifera*). Courtesy State University of New York College of Forestry.

¹¹ Taken from "Atlas of Paper Making Fibres," C. H. Carpenter and L. Leney, State U. of New York, College of Forestry, Syracuse, N. Y.

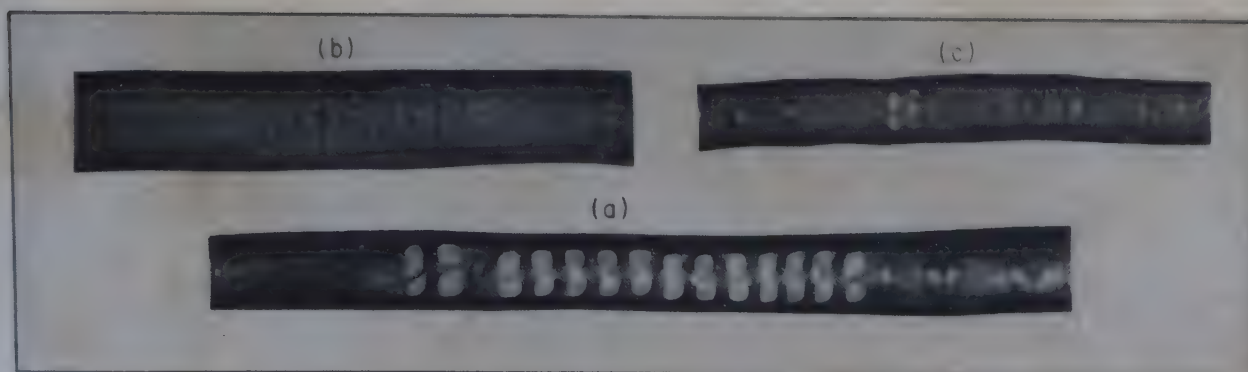


Fig. III-3. Portions of tracheids depicting typical ray crossings for several different softwoods: (a) western white pine (*Pinus monticola*), a soft pine; (b) sitka spruce (*Picea sitchensis*); (c) shortleaf pine (*Pinus echinata*), a southern pine. Courtesy State University of New York College of Forestry.

are shown in Figure III-3.¹² It is evident, for example, that pine and spruce can be readily distinguished, since the pits, in the case of pine, are large and rectangular, whereas those in spruce are smaller and slit-like. Striations in the cell wall, which are due to cell wall thickening, help in the identification of Douglas fir. In some cases, extreme beating or chemical degradation of the fibers may obliterate the identifying features, but in most samples of pulp or paper, the identifying characteristics are readily apparent. The use of ink as a fiber stain sometimes aids in identification.

Physical Properties of Wood

Some of the physical properties of wood of importance to the pulp and paper chemist are density of wood, moisture content of wood, proportion of heartwood to sapwood, and ratio of springwood to summerwood. These are discussed below.

Density of Wood

Density (or specific gravity) is an important factor in determining the yield of pulp obtained from a given wood, either in terms of yield of pulp per individual digester, or yield of pulp per cord of wood. Wood of low density results in a low yield of pulp per cord of wood and a low yield of pulp per digester, regardless of the yield obtained per unit weight of wood. Furthermore, increased density generally means increased pulp strength, so that high density is desirable both from the standpoint of improved pulp quality and from the standpoint of reduced manufacturing cost. Uniform density is very important for certain pulping processes.¹³

Density is a fairly inherent characteristic of wood, although there is a marked variation of density with the age, geographical location, and growth

¹² Taken from "Atlas of Paper Making Fibres," C. H. Carpenter and L. Leney, State U. of New York, College of Forestry, Syracuse, N. Y.

¹³ O. Maass and R. de Montigny, *Dominion Forest Service Bull.* 87, Canadian Dept. of Interior, Ottawa (1935)

conditions of the wood. In general, the different species may be grouped into (1) low-density woods, which include the softwoods (e.g., spruce and hemlock), and certain low-density hardwoods (aspen and cottonwood), which have a density of about 22 to 24 lb./cu.ft., and (2) the high-density woods, which include certain hardwoods (e.g., birch and beech), which have a density in the neighborhood of 34 lb./cu.ft. In the case of spruce and balsam, the specific gravity is about 0.33 to 0.45 (average around 0.4), which corresponds to wood weight per cord of 2,059 lb. and 2,808 lb., respectively, on the basis of a solid volume per cord of 98 cu.ft.¹⁴ The specific gravity of wood is only about one-third that of pure cellulose, which attests to the highly cellular and porous nature of wood.

Since wood expands and contracts with variations in moisture content, specific gravity must be measured in terms of specific moisture content and volume. Specific gravity is generally based either on moisture-free weight per maximum (green) volume, or moisture-free weight per minimum (dry) volume. Maximum (green) volume, which is the volume obtained when the wood has a moisture content in excess of 20 to 32% (the fiber saturation point), is determined by soaking selected disks of the wood in water until thoroughly swelled and then weighing by displacement in water. This is the most convenient basis on which to express specific gravity since it permits ready computation of weight per unit of volume at any moisture content. Minimum (dry) volume is determined by drying disks of the wood, dipping in hot paraffin, and weighing by displacement in water. The moisture-free weight of the wood is obtained by drying the wood for 24 to 48 hours, or until constant weight is obtained. If desired, wood chips may be used in place of disks for making these measurements.

Moisture Content of Wood

Freshly cut wood has a high moisture content, the cell walls are saturated with water and at least some of the cell cavities are full. As the wood is dried, no shrinkage takes place until the moisture content falls below the fiber saturation point, which varies, depending upon the species, but is usually between 20 to 32% moisture. The shrinkage is greatest in the tangential direction, less in the radial direction, and practically non-existent in the longitudinal direction.

The amount of moisture in wood at the time it is received at the mill varies, depending upon the species, season of the year, and the time of seasoning. Thoroughly air-dried wood may contain as little as 12% moisture, but some woods dry out much more slowly than others, so that the time of seasoning is no criterion. Moisture in wood is usually determined by the toluene distillation method.

¹⁴ J. B. Jones, *Tappi* 32, No. 2: 58-62 (Feb., 1949)

Most analytical results on wood are reported on the moisture-free basis, which makes it necessary to know the moisture content. Moisture content is an important factor in pulping, since it affects the packing of the chips in the digester and the concentration of the cooking chemicals added. Seasoning is important, since green wood generally produces pulp of higher strength and yield than wood which has aged for long periods of time because of the degrading influences of time, weather, insects, and microorganisms. Green softwoods are, however, more likely to cause pitch trouble than aged softwoods.

Heartwood and Sapwood

Sapwood consists of the fibers of comparatively recent growth located in the outer layers of the tree. Heartwood consists of the older fibers in the center of trees. In most species, there is a marked difference in properties between heartwood and sapwood, although in some species (e.g., fir), there is comparatively little difference.

For determining the relative volumes of heartwood and softwood in pulpwood,¹⁵ special disks are cut from sample logs and planed to give smooth surfaces on both sides. Two radii are drawn on the surface of the disk at right angles to each other and passing through the center, and on these radii, the diameter of the heartwood and the total diameter of the disk inside the bark are measured. In many cases, it is very difficult to distinguish the heartwood from the sapwood, and special technique will be needed to establish the separation. This can be done by wetting the surface of the disk with soap solution and blowing compressed air against the opposite side of the disk so that bubbles appear in the sapwood area, but not in the heartwood area. The measured diameter of the heartwood area in any one disk can be denoted by d , and the measured diameter of the entire disk by D . The percentage of the volume of heartwood to the volume of the sum of the heartwood and sapwood is then given by the formula:

$$d^2/D^2 \times 100 = \text{Per cent heartwood}$$

In determining the average of the percentage of the volume of heartwood in a series of disks, an error will be introduced if the arithmetic average of the percentages from the various disks is taken, due to the varying sizes of the disks. A more accurate average will be obtained if the sum of the d^2 of the several disks is divided by the sum of the D^2 of the several disks, and the resulting ratio multiplied by 100. In this case, the average obtained is weighted by the areas of the several disks.

Sapwood is a more desirable part of the tree for pulping than the heartwood. It is generally much lighter in color, has a lower density, a higher degree of permeability, and generally contains a lower percentage of lignin,

¹⁵ U. S. Forest Products Laboratory, Method 113, Madison, Wis. (June, 1935)

ash, resins, gums, minerals, and other extraneous materials. In some of the softwood species, the sapwood may have a higher moisture content than the heartwood.

Springwood and Summerwood

Within each annual growth ring, there are usually two distinct zones of wood, the inner zone, or springwood, and the outer zone, or summerwood. The springwood fibers are produced during the early part of the growing season when growth is rapid, and the cells produced have thin walls. Summerwood fibers are produced later in the growing season when growth is slower, and consequently, the cells have thicker walls and smaller diameter. The amount of springwood and summerwood depends upon the growing season and the species. Some of the southern pines may contain as much as 60% summerwood fibers.

In those species where there is a pronounced contrast between the springwood and summerwood areas (e.g., pine and Douglas fir), there is likely to be a pronounced difference in the density and other properties of the wood in the two areas. With some species of pine, the summerwood fiber walls may be twice as thick as the springwood fiber walls, and the fibers may be as much as five times stiffer in water than the springwood fibers.¹⁶

Because of their thinner walls, springwood fibers are weaker and more readily beaten than summerwood fibers, and as a result, produce papers of high density, smooth surface, and high strength, whereas summerwood fibers tend to produce coarse, bulky papers.¹⁷ Springwood fibers appear in collapsed condition in beaten pulps in contrast to the inflated shape of the stiffer summerwood fibers. Springwood fibers contain a higher percentage of lignin than summerwood fibers, but summerwood fibers are coarser and darker in color, and generally have the higher bleach requirement.^{18, 19} The effect of springwood and summerwood fibers on the properties of paper is discussed later in the chapter on fiber bonding.

Minor Chemical Components of Wood

Wood contains five principal materials, cellulose, hemicellulose, lignin, mineral matter, and extractives. The first three of these, cellulose, hemicellulose, and lignin, have already been discussed. The following section is devoted to a discussion of the minor components of wood, the mineral matter and that class of substances grouped under the title of extractives.

¹⁶ C. O. Seborg and F. A. Simmonds, *Paper Trade J.* 113, No. 17: 225-226 (Oct. 23, 1941)

¹⁷ G. J. Ritter, *Paper Trade J.* 101, No. 18: 264-272 (Oct. 31, 1935)

¹⁸ G. J. Ritter and L. C. Fleck, *Ind. Eng. Chem.* 15, No. 10: 1055-1056 (Oct., 1923)

¹⁹ G. J. Ritter and L. C. Fleck, *Ind. Eng. Chem.* 18, No. 6: 608-609 (June, 1926)

The extractives in wood are generally considered to be those materials soluble in "neutral" solvents, such as ether, alcohol-benzene, and water. They generally amount to 3 to 8% of the wood weight and include such materials as oils, resins, waxes, fats, tannins, sugars, starches, dyestuffs, pectins, proteins, gums, and organic acids. Extractives do not form part of the wood cell wall structure, but rather occur in the cell cavities.

Ether extract is obtained by extracting sawdust in hot ethyl ether for 6 to 8 hours. The extract contains resins, fats, fatty acids, oils, waxes, resenes, and sterols (crystalline alcohols). The alcohol-benzene extract is obtained by extracting ether-extracted wood in a mixture of alcohol (33 volumes) and benzene (67 volumes) for 6 to 8 hours. This extract contains the tannins, essential oils, phlobaphenes, and certain of the waxes, fats, and resins which are not soluble in ether. The water extract is obtained by digesting finely ground wood in water at 23° C. for 48 hours. This extract includes the soluble carbohydrates, salts, pectin-like materials, certain coloring agents, phlobatannins, and certain acids (by hydrolysis).

All the above extraction methods are in wide use in wood analysis. However, the methods are of little value in indicating the chemical composition of wood, since the results cannot be correlated with definite components of the wood, and furthermore, the results depend to a large extent upon the species used. The most important use for these extraction methods is to remove extraneous materials from wood prior to making determinations for cellulose and lignin content.

Resins and Waxes

Coniferous woods (softwoods) usually contain appreciable amounts of resinous matter, fats plus resins, which show up as a high ether extract. The amount of this resinous matter in spruce and hemlock is generally less than 1.0%, while that of the pines generally runs from 2 to 6%. The resins are mainly oleoresins and terpenes. The resin acids vary in composition, but there are two types of acids, the abietic and the pimaric types. The abietic acids are subject to oxidation due to their conjugated double bonds, but the pimaric acids are not. The fatty acids (mostly oleic and linoleic) are combined with glycerin in the form of esters.

The resin content is generally greater in the heartwood than in the sapwood. In the case of pine, the sapwood is reported to be rich in fatty acids, whereas the heartwood is rich in resinous acids.²⁰ In pine heartwood, the resin content sometimes reaches a high of 20 to 25%. As a general rule, the hardwood species have a lower resin content than the softwoods, which shows up in a lower ether extract. Hardwoods, however, contain

²⁰ H. Bergstrom and K. G. Trobeck, *Svensk Papperstidn.* 50, No. 9: 215-221 (May 15, 1947)

an appreciable amount of alcohol-soluble material consisting of waxes, gums, and fats, principally the glyceride of oleic acid.

Resins in wood are objectionable from the papermaking standpoint, since they cause trouble (principally in sulfite and groundwood pulps) by forming pitchy deposits on the paper machine. If left in the pulp, they tend to cause discoloration of the paper on aging.²¹ In certain pulping processes (sulfate process), the resins and fatty acids are recovered in the form of tall oil.

The resin, wax, and fat content of the different species varies considerably according to the geographical location and season of the year. It has been stated that the fatty acid content is highest in the spring. Aging of the wood after cutting changes the resin by oxidation from a tacky substance to a considerably less sticky material. Hibbert and Phillips²² found that seasoned jack pine has a lower percentage of fats, but a higher percentage of resin acids than the unseasoned wood, which is in agreement with the common belief that it is the ether extract (fatty material) which is most troublesome in causing pitch trouble on the paper machine. Often, the total amount of extract is reduced by storage. The conditions under which the aging, or seasoning, is carried out is important. For example, aging the wood in chip form for two weeks is equivalent to aging for 6 months to a year in log form.²³

Much of the resin content in the original wood is located in small cells, called the parenchyma cells which form a large part of the so-called fines of ordinary pulp. It has been found that a removal of these fines from paper-making pulp by screening will greatly reduce the resin content of the pulp.

Tannins

Tannins are a group of closely related compounds found to a small extent in most woods and to an appreciable extent in eastern hemlock, chestnut, oak, and a few of the western coniferous species. Chestnut contains from 9 to 16% tannin, most of which is in the heartwood. Tannin is present in the bark of hemlock and oak to the extent of 6 to 11% of the bark weight.

Tannins are soluble in water and usually are removed from the wood in the pulping liquor. In some cases, particularly with chestnut and oak, the wood may be profitably extracted with water before pulping at slightly under 100° C. to remove the tannins for sale. The extracted wood can then be used for pulping (generally by the semichemical and the soda processes). Extraction is economical only with those woods which average

²¹ J. C. Tongren, *Paper Trade J.* 107, No. 8: 76-84 (Aug. 25, 1938)

²² J. B. Phillips, *Pulp Paper Mag. Canada* 31, No. 6: 211-219 (Feb. 5, 1931)

²³ L. E. Fitzgerald, *Paper Trade J.* 103, No. 17: 266-268 (Oct. 22, 1936)

about 5% tannin or better. The liquor which is obtained by leaching is evaporated to approximately 50% total solids and is sold to leather manufacturers. The concentrated liquor contains about 65 to 80% pure tannin, together with other materials such as sugars, mineral salts, organic acids, and degradation products of tannin.

Tannins are amorphous substances which range in color from a light straw to a dark reddish brown. True tannin is believed to be an ester of glucose and tannic acid (also called gallotannin or digallic acid). The ester is subject to hydrolysis in acid medium and is a strong reducing agent. Some of this true tannin is present in wood, but wood tannin is a mixture of several different substances. Phlobatannin, which is present in high percentage, does not contain sugar in its formula and is not hydrolyzed by acids, but instead condenses to products of high molecular weight and is slowly precipitated from solution in acid medium. The insoluble polymers are known as phlobaphenes.

Dyestuffs

All wood contains a small percentage of organic coloring matter, especially West Coast woods. Some of the known coloring agents in wood belong to the catechins, flavonols, naphthoquinones, xanthenes, and anthocyanins. The coloring matter in wood is partially removed in pulping, but some coloring matter remains with the pulp. This is responsible for the darkening of pulp which occurs upon exposure to air. Most of this coloring matter is removed when the pulp is bleached, but the coloring matter in certain species is quite difficult to remove.

Pectins

True pectin consists of polygalacturonic esters of arabinose and galactose. Wood contains some true pectin, as well as pectin-like materials. The pectin content of wood is greater the younger the wood and is generally higher in the hardwoods than in the softwoods. However, it is usually less than 1 to 1.5% of the weight of the wood.

Mineral Matter

Part of the mineral matter in wood shows up in the water extract. The total mineral content of wood is obtained by an ash determination.

Much of the mineral matter in wood is held in a strongly adsorbed condition or combined with organic or inorganic matter in an insoluble form. Calcium, potassium, and magnesium usually make up the bulk of the metallic elements, but sodium, iron, aluminum, and manganese are always present. The metals are usually in the form of carbonates, phosphates, oxalates, or sulfates. Silica is also usually present. The ash content of wood generally runs from 0.2 to 1.0%.

Alkali Solubility

A common test on wood is the 1% alkali solubility test. This test is carried out by digesting 2 g. of sawdust (passing a 40-mesh screen and retained on a 60-mesh screen) in 100 ml. of 1% sodium hydroxide solution on a water bath at 97 to 100° C. for exactly one hour with three stirring periods. After filtering and washing with hot water and 10% acetic acid solution, the residue is weighed and the per cent soluble matter is calculated.

The 1% alkali solubility test is not a test for extractives, since it removes lignin, pentosans, and hexosans, as well as some of the resin acids and tannins. The principal use for this test is to determine the extent of wood decay. Decayed wood is undesirable for pulping, since it has a lower density, results in lower yields of pulp, and produces pulp having lower strength, darker color, and lower alpha cellulose content than sound wood.²⁴ The loss in pulp yield and pulp quality resulting from decay is proportional to the increase obtained in the 1% alkali solubility test.²⁵ The effect of decay on the chemical composition of Douglas fir is shown in Table V.²⁶

TABLE V
EFFECT OF DECAY ON PROPERTIES OF DOUGLAS FIR

	Sound wood	Partial rot	Complete rot
Cold water solubility, %	4.03	1.75	1.16
Hot water solubility, %	6.26	5.94	8.93
Alkali solubility, %	20.29	46.37	77.13
Cellulose, %	58.96	41.66	8.47
Pentosans, %	7.16	6.79	2.96
Methyl pentosan, %	2.64	3.56	6.06
Methoxyl, %	3.94	5.16	9.09

Wood decays less in cold weather than in warm weather, owing to the inhibition of microbiological growth at low temperatures. The moisture content of the wood is a factor in decay, since wood containing less than 20% moisture or more than 60% moisture is practically immune to decay. Wood which is submerged or floated in water decays very slowly because of the limited supply of available air. The estimated deterioration of wood on storage for five years varies from about 35% for storage in block piles to about 12% for storage in water.²⁷ Balsam deteriorates faster than spruce, with black spruce holding up slightly better than white spruce.

The most effective way of preventing decay is by stacking the wood on sites which are clean, well drained, and well ventilated. Barking of the

²⁴ G. B. Creamer, *Pulp Paper Mag. Canada* 51, No. 4: 86-90 (Mar., 1950)

²⁵ O. D. Anderson, *Paper Trade J.* 104, No. 6: 70-72 (Feb. 11, 1937)

²⁶ R. E. Rose and M. W. Visse, *Ind. Eng. Chem.* 9: 284 (1917)

²⁷ TAPPI Data Sheet 150 (Dec., 1948)

wood before storage helps to reduce decay. One precaution sometimes taken to prevent the decay of stacked wood is spraying of the wood with water to keep the moisture content high. All decayed wood should be eliminated from the shipment before storage, the yard should be carefully cleaned when new wood is brought in, and a bed of cinders or crushed stone should be used as a base. Burnt or fire-marked wood should be removed, since carbonized material may find its way into the finished pulp. Piles of pulpwood should contain no more than about 20,000 cords of wood in order to reduce the fire hazard.

History of Wood

The history of wood furnishes valuable information concerning the usefulness of wood for pulping purposes. In so far as the data are available, it is desirable to have the following information on each wood shipment: (1) geographical location of stand from which the wood was taken; (2) site factors influencing growth (altitude, soil, and climate); (3) type of stand (virgin growth, second growth, or reforested); (4) part of tree from which bolts were taken (stump, bole, tops, or branches); (5) condition of wood (soundness as affected by fire or fungus attack); (6) type of material (whether barked or unbarked, whether round or split, whether in form of bolts or manufacturing waste); (7) any abnormal characteristics.

Most of the above information can be obtained only from the supplier of the wood, and definite arrangements should be made to obtain as much of this information as possible at the time the order is placed. For commercial purposes, it is unnecessary to obtain as full and complete a history as outlined above, but nevertheless, it is often desirable to learn as much as possible of the source of the wood used. It has been found in some cases that the wood obtained from certain sections will give substantially higher yields of pulp per cord than will wood from other sections, the wood in both cases being of the same species. When such variations are discovered, it is obviously to the advantage of the mill to restrict purchases of wood to those sources having demonstrated advantages from the standpoint of cost or quality.

Conditions of Growth

It is well known that conditions of growth (altitude, soil type, exposure, etc.) influence the properties of wood which, in turn, influence the quality of the pulp which can be obtained from the wood. In extreme cases, more so with softwoods than with hardwoods, differences in growth conditions may result in a greater difference within a given species than normally exists between different species. In Sweden, wood is sometimes

graded according to the place of growth, and this is one of the reasons responsible for the high quality of Swedish pulp.

Rate of growth affects the quality of pulpwood. Experience has shown that slow-growth wood has a smaller diameter, higher density, and a higher lignin content than fast-growth wood.²⁸ Because of the higher density, greater yields per cubic foot of solid wood and per cord of wood are obtained from slow-growth wood than from rapid-growth wood.²⁹ However, fast-growth wood can be pulped by the mechanical process with lower power consumption than slow-growth wood, and the pulp has better strength, better color, and less pitch.³⁰ Chemical pulp made from rapid-growth wood is generally higher in tearing strength but lower in bursting and tensile strength than pulp made from slow-growth wood.

The rate of growth (radial) can be measured on sample disks of the wood by drawing several lines passing through the center, marking off on each radius successive intervals of 1 in., and counting the number of annual rings in each interval. From this, the average rate of growth in inches per year, or the volumetric rate of growth in cubic feet of wood per year per foot of length, can be computed.³¹

The average age of wood, which is generally reported as the arithmetic average of the annual rings in sample disks taken from the sample cord, is known to be an important factor in wood evaluation. C. H. Herty's well-known work on southern pine showed that young new growth of pine is light in color, free from heartwood, and contains less pitchy material than old growth, a discovery which was one of the factors giving an impetus to the southern paper industry. The same situation exists in the case of jack pine in the northern states, where it is well known that old, slow-growth jack pine does not pulp as well as young, fast-growth pine. In general, pulp yields are lower for old wood than for young wood.

Part of Tree

Wood fibers vary according to their position in the tree. The lignin content is high in the wood at the base of the tree and low in the wood at the top of the tree. The branches are relatively high in lignin content.

In coniferous woods, the fibers increase in length in each succeeding growth ring up to about the fiftieth year. Fiber length also increases with increase in height level to a definite maximum point (about 10–20 ft. from the ground), after which fiber length decreases with further increases in

²⁸ G. J. Brabender, *Tappi* 32, No. 8: 337–339 (Aug., 1949)

²⁹ G. H. Chidester, M. W. Bray and C. E. Curran, *Paper Trade J.* 109, No. 13: 170–176 (Sept. 28, 1939)

³⁰ C. E. Curran, *Paper Trade J.* 103, No. 11: 200–204 (Sept. 10, 1936)

³¹ U. S. Forest Products Laboratory, Method 113, Madison, Wis (June, 1935)

height. Fiber length is distinctly less in the branches than in the bole. The density, summerwood content, and heartwood content of the wood generally decrease with increasing height.³²

Because of the above differences, logs taken from the top, middle, and butt of the tree produce pulps differing in yield and quality.³³ The cellulose content of the pulp and the pulp yield generally decrease in going from the butt to the top logs.³⁴ Pulps having the highest bursting strength are obtained from the top logs, but the tearing strength is sometimes lower, due presumably to the higher springwood content of the top logs.³⁵ Wood from the branches produces pulp of lower yield and lower strength than wood from the trunk of the tree.³⁶

Abnormal Wood

Abnormal wood is often present in commercial pulpwood. This wood affects the quality of the resultant pulp, and in some cases, abnormal wood in a given species may produce pulp as widely different in strength, yield, and bleach requirement as would be obtained from two different species.

Compression wood, which frequently occurs in coniferous species in the lower sides of the trunk of a leaning tree or where the tree is exposed to excessive wind action, is distinguished by eccentric annual growth rings containing fibers which are approximately 70 to 80% of the length of normal wood fibers.³⁷ The fibers have very thick walls and high lignin content and are undesirable for papermaking because of their brittleness, which causes them to break into small fragments, particularly in the mechanical pulping process. Compression wood does not differ chemically from normal wood, but the difference in physical properties results in pulps of low yield, poor strength, and dark color.^{38, 39}

³² G. H. Chidester, M. W. Bray and C. E. Curran, *Paper Trade J.* 109, No. 13: 170-176 (Sept. 28, 1939)

³³ J. N. McGovern and G. H. Chidester, *Paper Trade J.* 106, No. 23: 317-319 (June 9, 1938)

³⁴ J. N. McGovern and G. H. Chidester, *Paper Trade J.* 106, No. 23: 317-319 (June 9, 1938)

³⁵ J. N. McGovern and G. H. Chidester, *Paper Trade J.* 106, No. 23: 317-319 (June 9, 1938)

³⁶ E. Häggglund, *Paper Trade J.* 81, No. 2: 11-13 (July 9, 1925)

³⁷ M. Y. Pillow, E. R. Schaefer and J. C. Pew, *Paper Trade J.* 102, No. 16: 220 (Apr. 16, 1936)

³⁸ T. R. Moore and F. H. Yorston, *Pulp Paper Mag. Canada* 46, No. 3: 161-164, Sixth Wartime Issue (1945)

³⁹ C. E. Curran, *Paper Trade J.* 103, No. 11: 200-204 (Sept. 10, 1936)

PULPING

Introduction to Pulping

Pulp preparation is the beginning phase of paper manufacture, since it is impossible to produce paper without first reducing the raw material to the fibrous state. The first basic step in pulp preparation is pulping. This consists of cooking the raw material, usually wood, in suitable chemicals in a digester under controlled conditions of temperature, pressure, time, and liquor composition, or reducing the raw material to the fibrous state by mechanical or semimechanical means. The second basic step is pulp purification, whereby the pulp is subjected to bleaching and purifying agents to render the pulp more suitable for its intended use.

The properties of pulp and the paper made from it are determined in the pulping process. Whether the paper mill is attached to the pulp mill or buys its pulp separately, successful operation of the mill depends upon a continuous supply of suitable quality pulp. In this chapter, the various pulping processes are described. The engineering features of the pulping processes are not covered, but an attempt has been made to cover the fundamental chemical details of the various processes so that the chemist will have an understanding of the nature of the different commercial pulps.

Types of Pulping Processes

Pulping processes are of three principal types, mechanical, chemical, and semichemical. The mechanical process involves the reduction of wood or other raw material to the fibrous state by mechanical means, generally by grinding wood to a pulp against a large grindstone. The chemical process involves a cooking of the wood with chemicals which selectively remove lignin and other impurities, isolate, and partially purify the individual fibers. There are three major chemical processes of commercial importance, namely, the soda, sulfate, and sulfite. The semichemical process involves an initial treatment for softening the wood, followed by mechanical reduction to the fibrous state. The initial treatment may vary from a simple steaming of the wood to a more drastic treatment with chemical.

The chemical pulping of wood is described first because wood is the most important raw material. The mechanical and semichemical processes

of pulping wood are discussed after the chemical processes. Later a description is given of the cooking of rags, straw, and other special materials.

Recent Trends in Pulping

Within recent times, there have been several major advances in pulping processes. Perhaps the greatest forward step has been a broadening in the number of wood species used. The pines have become well established in the southern states as pulpwoods, even for fairly high-grade papers, while in both the northern and southern paper mills, there has been a notable increase in the utilization of hardwoods. The future of pulp mills in the northern states depends largely upon their ability to utilize hardwood species which constitute such a high proportion of the northern forest areas. In many areas, spruce and fir have been so completely cut that mixed hardwoods dominate the forest. In the lake states region, aspen, cottonwood, and birch are being used in increasingly large quantities, and there is increased usage of birch, beech, and maple in the northeastern states. The outcome should be a lessening in the proportion of softwoods which are removed and hence a more nearly balanced use of the forest. Similar problems exist in the southern states, although the situation is not nearly so serious as in the northern states because of the faster rate of growth of the southern pines. However, Young¹ lists the hardwood invasion of second-growth forests as the most important problem in the southern states, after fire. The trend in pulping today is to use whatever species are available and to adapt the cooking process to those species.

Another objective of modern pulp manufacture is to increase the yield of usable pulp from a given quantity of wood. Spruce, for example, contains about 65% total carbohydrate, and yet the average yield of pulp obtained from spruce by the sulfite process is only 45 to 47% for papermaking grades. This loss of carbohydrate becomes a matter of increasing concern as the cost of wood continues its upward trend. Important advances have been made recently in increasing the yield of pulps suitable for making coarse papers by using semichemical processes which produce pulps in yields of 60 to 80%. Recent developments in the bleaching of high-yield pulps have extended the usefulness of these pulps. An important development has been the use of bleached and unbleached groundwood pulps for printing papers, thus greatly increasing the usage of these pulps.

The development of dissolving grade wood pulp by the sulfite process and, to a limited extent, by the sulfate process, has been one of the most important advances in recent years. These pulps, although not used in papermaking, have yielded knowledge which has helped to develop better paper-

¹ V. Young, *Tappi* 32, No. 1: 1-5 (Jan., 1949)

making pulps. Both softwoods and hardwoods have been converted into high alpha pulps suitable for making viscose.

Chemical (Cooking) Processes

The cooking of wood is carried out in large metal digesters. The wood is first barked, chipped, and then loaded into the digester. Means are provided for adding the chemical. Heat is applied, and the cook is continued until the desired degree of purification is obtained. The cooking liquor may be acid (sulfite process) or alkaline (sulfate and soda processes).

Wood is a highly complex association of substances which include cellulose, lignin, and hemicelluloses. Of these substances, cellulose is most resistant to chemical attack. During cooking, the chemical reacts with the lignin in the wood, forming soluble compounds which can be removed by washing. Cooking is often described as delignification. In the bleachable grades, over 95% of the lignin is removed. In the case of easy bleaching sulfite pulp, less than 1.5% lignin is left in the pulp. However, the term "delignification" is not accurately descriptive of the cooking process, inasmuch as other substances are removed, such as the less resistant carbohydrates, resins, and mineral matter. In fact, during the early stages of cooking by the soda process, carbohydrates are more rapidly removed than lignin.² It is exceedingly difficult to remove one constituent of the wood without removing or drastically altering some of the other constituents. Even chlorination, followed by extraction with weak alkali, which is considered to be a most specific reaction for lignin, removes some hemicelluloses from wood.³

In the initial period of the cooking cycle, the middle lamella, which cements the fibers together and consists mainly of lignin, is attacked and solubilized,⁴ thereby loosening the individual fibers. The results obtained depend upon the type of cooking process, but in most cases, part or all of the primary wall is removed, and in the case of highly cooked pulps, a substantial amount of the lignin is removed from the secondary wall. Within a given cook, the effect is not the same on all the fibers, since conditions in the same digester vary from mild to severe, with the result that the average commercial pulp contains some overcooked and some undercooked fibers. Certain portions of the wood, such as the medullary rays and epithelial tissue, may remain relatively unattacked, or only partially attacked, during cooking.

² F. E. Brauns and W. S. Grimes, *Paper Trade J.* 108, No. 11: 136-139 (Mar. 16, 1939)

³ W. M. Harlow, *Paper Trade J.* 109, No. 18: 242-246 (Nov. 2, 1939)

⁴ C. W. Carpenter and H. F. Lewis, *Paper Trade J.* 99, No. 3: 37-42 (July 19, 1934)

It should be pointed out that the wood chips retain their original shape during cooking, and it is not until they are discharged from the digester that they are broken up. Blowing of the digester must not be done at too high a pressure, since this has a drastic effect on the pulp and results in loss of steam and chemical (sulfite process). The progress of the cook can be followed (1) by analysis of the cooking liquor, (2) by comparing the cooking liquor with color standards, or (3) by the permanganate number of the pulp.

The final cooked pulps are classified as "soft" or "hard," depending upon the severity of cooking. In general, pulps which are classified as "soft" are well cooked, are of high purity, and have good tearing strength, low bursting strength, and relatively low bleach consumption. Pulps classified as "hard" are of low purity and have high bursting strength and high bleach consumption. The degree of cooking is generally measured by tests which are indirectly related to the lignin content of the pulp, such as bleachability tests (permanganate number). There is an optimum bleachability value for each grade of pulp. If this value is much higher than the optimum, excess bleach will be required in the bleaching operation, whereas if the bleachability value is lower than the optimum, indications are that the pulp has been overcooked. Pulps of very high bleachability, i.e., unbleached pulps containing high percentages of lignin (5% or more), are likely to be stiff and difficult to beat; they tend to break down, rather than undergo typical beating. Complete purification is not, however, necessary in the cooking process, since final purification can be obtained in the bleaching process under milder conditions which are not so degrading to the fiber.

Acid cooking liquors (sulfite process) and alkaline cooking liquors (soda and sulfate process) differ in the rate of lignin removal, amount of cellulose degradation, amount of hemicellulosic material removed, and in other actions. Each process is described separately later on.

Variables in Cooking

In commercial cooking, reagents are selected which are reasonably specific toward lignin, and conditions for cooking are chosen which give the optimum reaction with the lignin without excessive degradation of the cellulose. Among the variables in any cooking process for a given wood species, the five most important are: (1) temperature of cooking, (2) time of cooking, (3) ratio of active chemical to wood, (4) concentration of cooking liquor, (5) composition of cooking liquor. These are independent variables and have a direct influence on the results of the tests used to measure the chemical and physical properties of the final pulp (the dependent variables). Of the independent variables, the chemical-to-wood ratio, the concentration of cooking liquor, and the liquor ratio are usually used to denote the com-

position of the chemical-wood-water system. However, fixing any two of these variables will automatically fix the third, although any one can be treated as an independent variable.

The concentration of active chemical in the cooking liquor is the most important variable affecting the rate of reaction. In the commercial range the rate of reaction increases almost directly with the concentration of the active cooking agent. One of the reasons that the rate of reaction decreases toward the end of the cook is that the concentration of cooking agent is greatly reduced at this point because of the consumption of chemical by the wood during the early stages of cooking. The effect of the different cooking variables will be discussed separately for each of the commercial cooking processes.

Preparation of Wood

The felling, transporting, barking, and chipping of wood are important preliminary steps to the pulping operation. After the wood is felled, it is cut into lengths and shipped to the mill where it is kept in a wood pile near the pulp mill. Water transportation (by driving, towing in booms or rafts, or by barge) is still widely used, but rail and truck transportation are increasing. Water transportation is far less suitable for hardwoods than for softwoods. Log lengths of 4 or 8 ft. are used in the east, midwest, and south. In the far west where logs are larger, they are brought to the mill in 16- to 60-ft. lengths and are stored in water to facilitate handling.

Cleaning Wood. Most of the wood is received at the mill in the unbarked state. Therefore, the first step in wood preparation is barking of the wood, using abrasive, hydraulic, or mechanical barkers. In some cases, the wood may be barked by hand at the time of cutting by chiseling off the bark with a spud or by shaving with a draw knife.

Hardwoods present more of a problem in barking than softwoods. Freshly cut birch is very difficult to bark but can be barked readily in regular mechanical barkers after aging for one season. During a limited period in the spring (sap peeling season), certain hardwoods (e.g., poplar) may be barked by hand in the woods. If water transportation is used, aspen is best barked in the woods, but birch is best floated unbarked.⁵ Chemical treatment of wood with soluble arsenic salts during June and July has been suggested as a means of extending the sap peeling season and facilitating hand peeling of all species in the wood. This treatment has proved most effective on the softwood species, but so far there has been no widespread use.

One of the oldest types of abrasive barkers is the barking drum, which consists of a large, open-ended drum in which the logs are tumbled against one another to loosen and rub off the bark that passes out between openings

⁵ J. J. G. Cullin, *Svensk Papperstidn.* 53, No. 3: 51-58 (Feb., 1950)

in the drum sections. Water sprays are used to clean the wood and wash away the bark. After a retention time of 0.5 to 2.0 hours, the cleaned logs are continuously forced out the end of the barker. Drum barkers have the disadvantage of brooming the ends of the logs so that dirt becomes embedded unless a large amount of water is used to wash the bark and dirt away. Another abrasive type barker (Waterous or Thorne barkers) consists of several pockets in which the logs are rubbed against each other with a rolling motion imparted by the action of cams. The logs move from one pocket to the other while being sprayed with water. A 45-ft. drum barker 12 ft. in diameter would normally have a capacity of about 15 to 20 cords per hour or about 30 cords per hour in the stripping season. In order to facilitate the removal of bark, some mills soak the logs in a hot pond maintained at 90–120° F. prior to entry into the barker.

There are several different models of the hydraulic barker,⁶ all of which use the same principle of directing a jet of water through a nozzle at the log at pressures ranging from 400 to 1,500 p.s.i. The jet plays directly on the log perpendicular to the surface of the wood so that it explodes or blasts off the bark. Hydraulic barkers are particularly well suited to the barking of large logs of coniferous woods, such as those found on the west coast of the United States. The results are not so satisfactory on the smaller eastern conifers, on hardwoods in general, or on frozen wood. One of the principal advantages over other types of barkers is the reduction in waste.

Of several mechanical barkers, the most important are the knife barker and the chain barker. In the knife barker, the log is held against a revolving disk equipped with a number of knives which shave the bark off the wood. This type of barker is used in species which are very difficult to bark, such as birch and beech, but it is very wasteful of wood and often removes as much as 30% of the good wood. The chain barker (Astrom) is a Swedish barker in which the logs are passed between heavy chains wrapped around the log. The chains scrape and twist the bark from the wood.

Extra cleaning of the wood may be done by cutting out the bad spots with a router equipped with rotating head (woodpecker) and by boring out the knots when exceptionally clean wood is required. Extra cleaning is often necessary on wood for sulfite or groundwood, since high quality pulp cannot be made by these processes unless clean wood is used. Bark and knots are highly undesirable in the sulfite process, since they are not digested by the acid cooking liquor. MacLaurin and Van Allen⁷ list the following factors as representing the relative dirt-producing potential of different impurities when wood is cooked by the sulfite process.

⁶ L. E. Hill, *Paper Ind.* 31, No. 9: 1062–1066, 1073–1074 (Dec., 1949)

⁷ D. J. MacLaurin and A. M. Van Allen, *Paper Trade J.* 127, No. 22: 23–30 (Nov. 25, 1948)

Type of dirt	Factor
Bark	48
Black knots	13
Pin knots	4

Lower-quality wood can be used in the alkaline cooking process—the soda and sulfate processes—than in the sulfite process.

Chipping Wood. Wood for the chemical processes must be chipped into small pieces in a chipper before pulping in order to improve the penetration of the cooking chemical. The chipper consists of a large disk fitted with sharp knives which are lined up so that the disk is in balance. The logs are fed to the knives through a spout, and as the disk rotates at about 300 to 400 r.p.m., chips are sliced from the end of the log which is supported by the bedplate of the chipper. Some chippers are equipped with four knives, but these have largely been replaced by multiknife chippers equipped with 8, 10, or 12 knives, since the latter reduce bouncing and recoiling of logs in the spout.⁸ There should be sufficient weight of wood in the spout to prevent excessive recoil (“dancing”) of the wood during chipping. Chipper knives must be resharpened at intervals of about 4 to 10 hours, depending upon the type of wood being chipped and the type of steel in the knife.

The logs enter the chipper at an angle to the horizontal and at an angle to the chipper knives so that the wood is sliced at an oblique angle (in a combination of tangential and cross-section cutting). Cutting in this way requires less power than cutting at right angles. Furthermore, it increases the cross-sectional area of pores in the chips and reduces crushing of the wood and closing of the pores. There is always some crushing of the wood, however, and it has been estimated⁹ that crushing of the wood in chipping is responsible for a 10 to 15% loss in bursting and tearing strength when the wood is cooked by the sulfite process. The loss in strength which results in sulfite pulping from crushing of the wood has been attributed to the development of fine cracks in the lignified sheath around the fiber, thus exposing the inner parts of the fiber to strong cooking acid.^{10, 11} This leads to a very great loss of strength in some cases¹² as, for example, when dull chipper knives are used on wood of very high moisture content (e.g., 200–300%, as is common in the heartwood of western hemlock).¹³ Crushing seems to have much less effect when the wood is pulped by the sulfate proc-

⁸ C. R. Wardwell, *Paper Trade J.* 128, No. 25: 220–221 (June 23, 1949)

⁹ F. H. Yorston, “Studies in Sulfite Pulping,” *Dominion Forest Service Bull.* 97, Canadian Dept. of Mines and Resources, Ottawa (1942)

¹⁰ B. L. Grondal, *Pacific Pulp Paper Ind.* 13, No. 7: 12–16 (July, 1939)

¹¹ G. Jayme and L. Groggaard, *Cellulosechemie* 18, 34–48 (Mar., Apr., 1940)

¹² O. Bildt, *Svensk Papperstidn.* 15: 148 (1938)

¹³ B. L. Grondal, *Paper Mill News* 62, No. 34: 14–16, 20 (Aug. 26, 1939)

ess. However, according to McGovern and Chidester,¹⁴ the average fiber length is reduced by about 28% by normal chipping.

Power costs are the most important part of chipping costs. Power requirements vary according to the type of wood, size of log, size of chips, and condition of knives. Power requirements are generally less when chipping softwoods than when chipping hardwoods, as shown in Table I,¹⁵ giving the maximum horsepower per cubic foot per second for several different species.

TABLE I

Wood species	Horsepower per cubic foot per second
Douglas fir	296
Yellow pine	344
Black gum	362
Red oak	486

Chips from the chipper contain material ranging all the way from fines and sawdust to oversize chips, but about 60% or more of the wood should be cut to dimensions determined by the setting of the knives. Fines are considered as material passing a 3-mesh screen, but retained on a 6-mesh screen, and the material passing a 6-mesh screen is considered as sawdust. The amount of fines generally varies from 5 to 10%, and the amount of sawdust varies from 1.5 to 3.0%, depending upon the condition and setting of the chipper knives. Fines and sawdust are removed from the acceptable chips because they reduce the average fiber length and, if left in the chips, would increase the dirt content of the pulp and interfere with circulation of cooking liquor in the digester. For example, Keller and McGovern¹⁶ report that sawdust produces a pulp with 50 to 70% lower strength than normal chips when eastern hemlock is cooked by the sulfite process. The oversize chips and slivers (about 1.5–3.0%) are also removed by screening, and these are sent to a chip crusher or a rechipper where they are broken up, rescreened, and returned to the process. The acceptable chips are transported to bins over the digesters to which they are fed by gravity as needed.

The size of the acceptable chips after screening varies considerably. In the sulfite process, the aim is for an average chip of about $\frac{3}{4}$ in. in length, but chips are present ranging from less than $\frac{3}{8}$ to over $1\frac{1}{4}$ in. in length. Average chip length is calculated from the weighted average of the chips falling in the classes 0 to $\frac{1}{2}$, $\frac{1}{2}$ to $\frac{3}{4}$, $\frac{3}{4}$ to 1, 1 to $1\frac{1}{4}$, and $1\frac{1}{4}$ in. and over.

¹⁴ J. N. McGovern and G. H. Chidester, *Paper Trade J.* 99, No. 18: 227–232 (May 3, 1934)

¹⁵ H. B. Barrow, *Paper Trade J.* 129, No. 25: 499–500 (Dec. 22, 1949)

¹⁶ E. L. Keller and J. N. McGovern, *Pulp Paper Mag. Canada* 48, No. 7: 72–75 (June, 1947)

Short chips are desirable from the point of view of uniform penetration of cooking liquor, but short chips mean higher power costs in chipping, smaller average fiber length, and a smaller percentage of long fibers in the pulp. McGovern and Chidester¹⁷ found that increasing chip length up to $\frac{1}{2}$ in. resulted in an increase in fiber length and an increase in pulp strength when cooking western hemlock by the sulfite process, but that there was no appreciable advantage from a strength standpoint in using chips longer than $\frac{1}{2}$ in. It is very important to have chip length as uniform as possible. The thickness of the chips is also important. Chips which are too thin produce very poor pulps. Backman¹⁸ found that the strength of both sulfite and sulfate pulps increased markedly as the thickness of hand-prepared chips was increased from 0.5 to 1.0 mm. to 3.0 mm., although a further increase of about 3.0 mm. resulted in a loss in strength.

An important measure of chip quality is chip density, or pounds of dry wood per cubic foot of chips. Chip density is a necessary measurement for calculating the amount of wood which can be charged to the digester. Cooking costs are determined by chip density; since the pulp yield per digester varies with the chip density. Chip density is determined by weighing the amount of air-dry chips contained in a box of known capacity while the chips are subjected to a pressure equivalent to the average pressure to which they are subjected in the digester. Another method is to measure the volume displaced by water-soaked chips obtained by measuring the amount of water added to wet chips of known weight in a container of known volume.

SULFITE PULPING

The pulping process now known as the sulfite process was discovered in 1866 by Benjamin Tilghman, an American. The first commercial sulfite mill was established in Sweden in 1874 under the direction of a Swedish chemist, C. D. Ekman. Since about 1890, the sulfite process has been well established as a commercial pulping process and was the most important chemical pulping process until about 1937, when it was superseded in importance by the sulfate process.

The active cooking chemicals in the sulfite process are sulfur dioxide, sulfurous acid, and calcium bisulfite. The cooking liquor, called acid, is thus a solution of calcium bisulfite which contains an excess of sulfurous acid. The cooking liquor is made at the pulp mill by burning sulfur to sulfur dioxide and reacting the gas with limestone or milk of lime to produce a cooking acid of the desired composition and strength. Cooking is done

¹⁷ J. N. McGovern and G. H. Chidester, *Paper Trade J.* 98, No. 18: 227-232 (May 3, 1934)

¹⁸ A. Backman, *Finnish Paper and Timber J.* 28, No. 13: 200 (July 15, 1946)

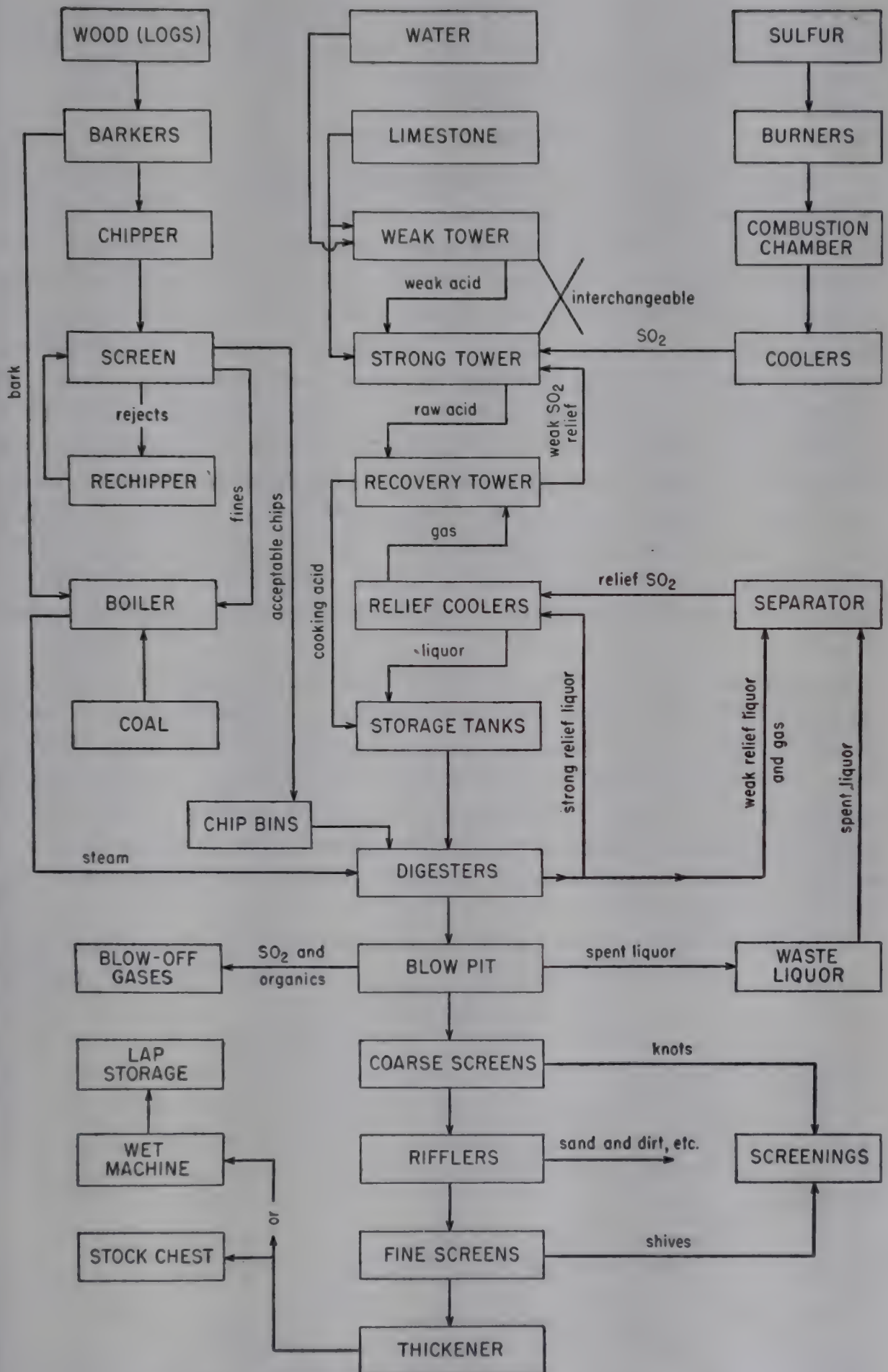


Fig. IV-1. Flow chart of the sulfite process (quick cook).

in acid-resistant brick-lined steel digesters or in stainless steel digesters with a capacity of about 10 to 35 tons of pulp. A flow chart of a typical sulfite mill layout is shown in Figure IV-1.

Preparation of Sulfur Dioxide

Sulfur dioxide used for making sulfite cooking liquor is prepared by burning pure sulfur in either rotary or spray burners in the presence of air. In the rotary burner, the sulfur is melted, and the molten sulfur (at about 260 to 300° F.) is vaporized at 600 to 700° F. and then is drawn into a secondary combustion chamber where sulfur dioxide is formed at temperatures of about 1600 to 1800° F. The speed of rotation of the rotary is regulated (about 1 R.P.M.) so that the entire inner surface is covered with burning sulfur. Primary air is added at same point and secondary air is added at the discharge end of the burner to provide sufficient air for the combustion of sulfur to sulfur dioxide in the combustion chamber. In the spray type burner (developed by Texas Gulf Sulfur Company), molten sulfur is delivered through steam-jacketed lines to atomizing spray nozzles which spray the molten sulfur into a furnace where it is burned at a temperature of about 1200 to 1500° C. in the presence of a controlled amount of air.

Commercial sulfur is very pure, generally containing about 99.9% sulfur on a dry basis. The only significant impurity is selenium which is undesirable because of its unfavorable catalytic effect in sulfur burning. Pyrites (iron sulfide) containing 35 to 40% sulfur are sometimes used, chiefly in Canada and in the Scandinavian countries, but the burning of pyrites is of relatively little importance in the United States. The burning of pyrites produces a gas somewhat lower in sulfur dioxide and oxygen than the burning of sulfur.

In the burning of sulfur in air, one volume of oxygen combines with one part of sulfur to yield one volume of sulfur dioxide. Since air contains 21% of oxygen by volume, it is theoretically possible to obtain a burner gas containing 21% of sulfur dioxide. The gas as it leaves the burner contains only about 15 to 17% sulfur dioxide (in some systems up to 19 or 20%), instead of the theoretical maximum (21%) which would result if it were possible to have complete control of the air and sulfur supply. The following equation expresses the air in cubic feet required at normal operating temperature:

$$\text{Volume air} = \frac{11.75}{\text{Per cent SO}_2 \text{ by volume}} = \text{cubic feet}$$

About 78 cu.ft. of air are required to produce gas having 15% sulfur dioxide by volume, compared to 62 cu.ft. of air for gas having 19% sulfur dioxide. Excess air about 10% greater than the theoretical amount is generally

used, but too much air should not be admitted, since this lowers the strength of the gas and favors the formation of sulfur trioxide. A small part of the air is admitted at the burner, the balance being admitted in the separate combustion chamber. The air should be dry, since moisture favors the formation of trioxide. High temperature (1000°C . or over) prevents the formation of sulfur trioxide by breaking down any trioxide which has formed into dioxide. Sulfur trioxide is undesirable because it is converted into sulfate in the final liquor. This reduces the strength of the pulp and tends to form a precipitate of calcium sulfate on the inside of the digesters. Free sulfur in the gas should be avoided, since this tends to precipitate the combined lime in the cooking acid.

The gas leaving the combustion chamber is about 700 to 1000°C . Because the solubility of sulfur dioxide in water decreases as the temperature increases, it is necessary to cool this gas to about 25 to 30°C . in the liquor-making plant. Rapid cooling of the hot gas is desirable to keep the formation of sulfur trioxide to a minimum; it is necessary to avoid temperatures in the range of 600 to 850°C . in which the rate of formation of sulfur trioxide is greatest. Both spray type and indirect type lead coil coolers are used, the former being best. Gerace¹⁹ reported that sulfur trioxide can be held to less than 0.03% by spray cooling.

The content of sulfur dioxide in sulfur-burner gas can be determined with the Orsat apparatus. The amount of sulfur trioxide in the gas can be determined by dissolving the gas in water, treating with an excess of 0.1 N iodine solution, and back-titrating first with 0.1 N thiosulfate solution and then with 0.1 N sodium hydroxide to a methyl red end point. The gas may also be analyzed in special analysis cells which measure the conductivity of the gas, either in the dry state or after dissolving in water.²⁰ In some systems, a sulfur dioxide controller is used to regulate automatically the flow of secondary air to the combustion chamber to maintain a uniform percentage of sulfur dioxide.

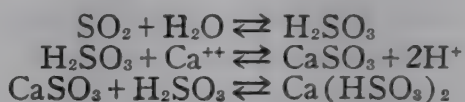
Preparation of Cooking Acid

There are two major stages in the preparation of sulfite cooking liquor: (1) The raw acid liquor making stage which comprises the absorption of cooled sulfur dioxide burner gas in water and the reaction of the resulting surfurous acid solution with milk of lime or limestone, and (2) the recovery process whereby the raw acid is fortified with relief gases from the digester until it reaches the desired strength for cooking. There are two principal systems for making raw sulfite cooking acid, the tower system and the milk of lime system.

¹⁹ T. Gerace, *Paper Trade J.* 124, No. 14: 57-58 (Apr. 3, 1947)

²⁰ J. B. Chandler, *Southern Pulp Paper Mfr.* 11, No. 9: 23-28, 65 (Sept. 15, 1948)

Tower (Jenssen) System of Making Bisulfite. In the Jenssen two-tower system, which is the system preferred by most American mills, the cooking acid is prepared by passing sulfur dioxide and water in countercurrent flow over calcium carbonate (rock limestone) resting on a grate in a large tower. The process is based on the fundamental laws of gas absorption. Cool sulfur dioxide gas is blown by means of a lead fan into the bottom of the first tower where it passes up through the limerock countercurrent to the water. The gas passing out the top of the first tower (strong-acid tower) is passed into the bottom of the second tower (weak-acid tower), and is again passed up through limerock. About 75 to 95% of the sulfur dioxide is absorbed in the strong-acid tower. The excess (tail) gas from the second tower is, in the case of most mills, blown to the atmosphere. Water is run in the top of the second tower in countercurrent flow to the gas. The following reactions are involved:



In the first stage of the above reaction sulfur dioxide gas comes into contact with water, forming sulfurous acid. The sulfurous acid then reacts with the limerock to produce calcium monosulfite, and since this is quite insoluble, it separates from solution. As the addition of gas continues, the monosulfite is converted into soluble calcium bisulfite. Conversion is complete at the point at which there is somewhat less than twice as much sulfurous acid as calcium oxide present.²¹ The final solution contains bisulfite, sulfurous acid, and free sulfur dioxide, and is known as raw acid solution. An excess of sulfurous acid is necessary at all times to keep the bisulfite in solution. Sulfite acid is very corrosive to iron and must be stored in wood or stainless steel tanks, and it must be used in digesters which are lined with acid-proof brick or other acid-resistant material. Stainless steel fittings and valves are generally used for handling the cooking acid, and there has been considerable interest recently in the use of stainless steel digesters.

Temperature is an important variable in determining the composition of the acid. In the summer months, it is difficult to absorb enough sulfur dioxide to obtain a cooking acid of the proper strength. High temperature favors solution of the limerock, but lowers the solubility of the gas, thereby increasing the combined sulfur dioxide but reducing the free sulfur dioxide. This can be partially counteracted by raising the grate in the tower, which increases the dissolved sulfur dioxide gas by allowing a longer period of contact with the gas and water at the base of the tower. According to Lund-

²¹ W. B. Beazley, H. W. Johnston and O. Maass, *Dominion Forest Service Bull.* 95, Canadian Dept. of Mines and Resources, Ottawa (1939)

berg,²² the best water temperature for acid making is 10 to 15° C., but most commercial operations are carried out at 18 to 28° C.

Milk-of-Lime System of Making Bisulfite. In the milk-of-lime system of acid making, sulfur dioxide gas is reacted with a milk-of-lime suspension. In one system, called the Barker system, there is high tower consisting of a perforated plate section and a packed section. The gas is first bubbled through the perforated plate section of the tower in countercurrent flow to a milk-of-lime suspension containing about 12 to 15 g. of calcium or magnesium hydroxide per liter. The resulting acid is then conducted from the lower plate through a control valve over a distributor plate and finally down through a section of packed tower where sulfur dioxide gas is absorbed to build up the free sulfur dioxide in the liquor. The tower system is generally operated under slight vacuum, in contrast to the Jenssen tower system which operates under pressure. A somewhat newer system, called the continuous (Kimberly-Clark) system, consists of two absorption towers, each tower containing four bubble compartments.

One important advantage of the milk-of-lime system of making acid is the good control which can be achieved. The concentration in the raw acid of soluble bisulfite (combined) can be readily controlled by varying the lime water concentration. On the other hand, milk-of-lime systems have a greater number of mechanical parts and are more likely to give trouble with corrosion and scale formation than tower systems. The quality of the lime is quite important in the milk-of-lime system, but any base can be used (unlike the tower system). High magnesium lime (dolomite) is preferred in the milk-of-lime system, because magnesium sulfite is more soluble than calcium sulfite, and there is less chance of clogging the holes of the tower plates.

Fortification of Bisulfite Liquor. When strong cooking liquors are required (5–6% free SO₂ or more), pressure towers are necessary to build up the concentration of free sulfur dioxide in the liquor. The true free sulfur dioxide concentration in solution is directly proportional to the equilibrium pressure of sulfur dioxide in the gas phase in accordance with Henry's law. In Figure IV-2, the solubility of sulfur dioxide in calcium bisulfite solution is shown for two different temperatures and various pressures, using a two-phase system (gas and liquid).^{23, 24} By maintaining a high partial pressure of sulfur dioxide in the gas phase, it is possible to build up a high concentration of free gas in the liquor.

Gas for fortifying raw acid may be burner gas compressed to 7 to 15 p.s.i. or relief gas from the digesters. Practically all sulfite mills fortify

²² A. H. Lundberg, *Pulp Paper Mag. Canada* 47, No. 10: 98–103 (Sept., 1946)

²³ Published in TAPPI Data Sheets

²⁴ C. K. White, J. E. Vivian and R. P. Whitney, *Tech. Assoc. Papers* 31: 141–143 (June, 1948)

their liquor with relief gases from the digesters, which means that part of the sulfur dioxide moves in a cycle in the pulp mill. There are two principal systems of fortifying the liquor, namely, the cold acid system and the hot acid (chemipulp) system. Generally about one half of the sulfur in the cooking liquor is sulfur that has been recycled through the system; only enough fresh sulfur is burned to make up for that part of the sulfur lost in the vent gases and spent cooking liquor.

In the cold acid system, the gases and hot liquor relieved from the digester may be passed to a separator where the gas is separated from the liquor. The cooled liquor is stored and later mixed with the weak acid. The

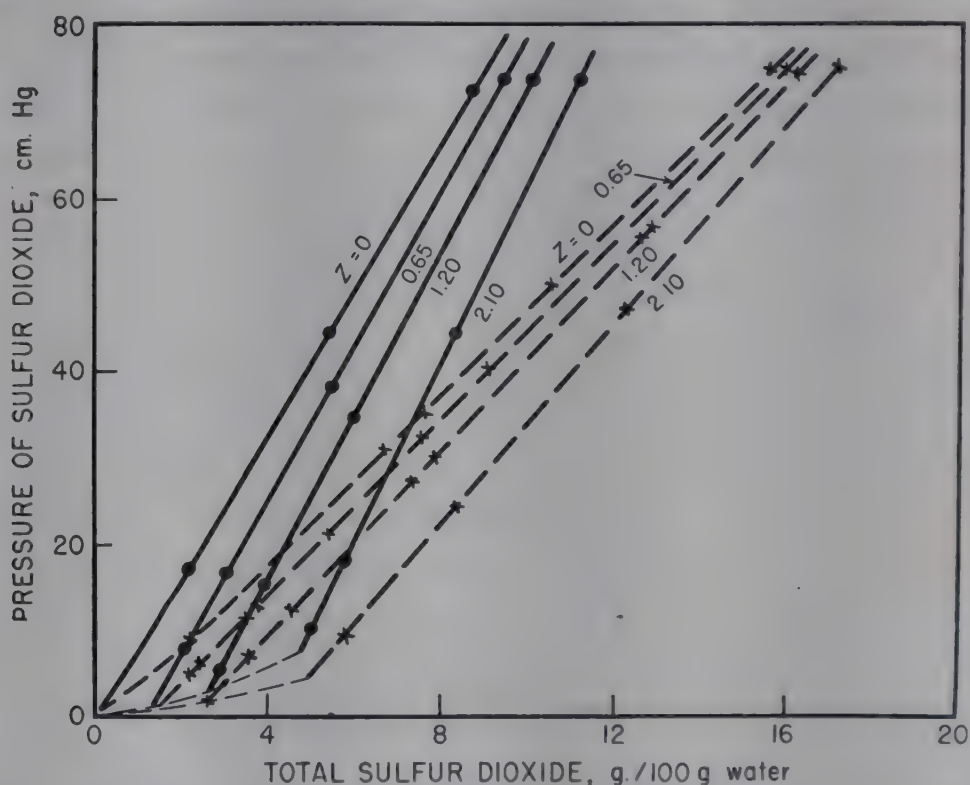


Fig. IV-2. Effect of pressure and temperature at 25° (—) and at 10° C. (---) on the solubility of sulfur dioxide in calcium bisulfite solution. The boundary of the three-phase system is shown by the curved dashed line in the lower left corner of figure. Z = grams combined sulfur dioxide per 100 g. water.

gas is cooled and absorbed in the strong acid from the acid plant in a pressure (recovery) tower filled with packing rings. The pressure in this tower is maintained at 7 to 20 p.s.i. so that the acid absorbs the relief gases and is fortified to the desired strength. The excess gas from the recovery tower is sent to the acid plant where it is mixed with burner gas entering the strong acid tower. The cold acid system has one serious disadvantage in that the heat in the relief is lost when the cooling water is run to the sewer.

To overcome the disadvantages of the cold acid system, another system known as the hot acid or chemipulp system has been developed. In this system, the heat in the digester relief is retained by introducing the hot re-

relief gases directly into the raw acid under pressure. The resulting hot acid is stored in a pressure vessel from which it is later pumped to the digester. In one form of the hot acid system, the relief gases and liquor from the digester are passed through a heat exchanger, and the gas is separated from the liquor. The liquor is added to the raw acid storage, and the gas is then absorbed in the hot cooking liquor in a special reclaimer, known as an accumulator, under pressure. The advantage of the chemipulp system is that the digesters are charged with hot cooking acid under pressure, the heat in the acid being that recovered from the digester relief. This process saves heat and improves the penetration of cooking acid into the wood chips. There are several variations of the chemipulp system, but in all of them, hot fortified acid is stored in accumulators at a temperature of about 70 to 85° C. and a pressure of about 30 to 50 p.s.i., depending upon the acid strength and temperature. Table II²⁵ shows the pressure which must be maintained in the accumulator for different temperatures and free acid strengths.

TABLE II

ACCUMULATOR PRESSURE REQUIRED TO MAINTAIN ACID CONCENTRATION
AT VARIOUS TEMPERATURES

Free sulfur dioxide, %	Pressure required at 40° C., p.s.i.	Pressure required at 60° C., p.s.i.	Pressure required at 80° C., p.s.i.
4	0	12.5	27.5
5	1.0	17.5	33.0
6	4.5	22.0	40.0
7	7.5	27.0	46.5
8	11.0	32.0	53.0

Accumulators may be old brick-lined digesters or vertical shells, but preferably they are spherical shells which hold from 1½ to 3 times the amount of acid used in an individual digester. In some systems, only one accumulator is used, whereas in other systems, two accumulators, a high- and low-pressure accumulator, are used. If two accumulators are used, the digester relief gases obtained in the early part of the cooking cycle are passed to a high-pressure eductor where the gas heats and fortifies the acid being pumped from the low-pressure accumulator and produces the strong hot acid which is stored in the high-pressure accumulator. (The eductor is an injector which mixes and absorbs the gas in the liquor as the liquor is passed through a nozzle into the drop leg of the high-pressure line, producing a suction which reduces the back pressure on the relief header.) The over gas from the high-pressure accumulator is used for heating and

²⁵ "Chemipulp Sulfite Mill Operation," Chemipulp Process, Inc., Watertown, New York

The amount of total, free, and combined sulfur dioxide in sulfite cooking liquor can be determined by volumetric analysis using the Winkler method. In preparing a sample for analysis, 10 ml. of liquor should be pipetted into a partially filled 100-ml. volumetric flask while the tip of the pipette is below the surface of the water, and then the flask should be filled to the mark. The various analyses are made as follows:

Total Sulfur Dioxide

A 10-ml. sample of the above prepared liquor is pipetted into 0.1 *N* iodine solution and the excess iodine is then titrated with 0.1 *N* thiosulfate, adding a small quantity of starch indicator toward the end of the titration. The difference between the original amount of 0.1 *N* iodine and the amount of 0.1 *N* thiosulfate used gives the number of milliliters of iodine equivalent to the total sulfur dioxide in the liquor.

$$1 \text{ ml. } 0.1 \text{ } N \text{ iodine} = 0.0032 \text{ g. } SO_2$$

If partially used liquor is being analyzed, high results may be obtained by the above method, due to matter removed from the wood. In such cases, a second determination should be carried out by adding to the flask about 5 ml. of iodine solution less than that consumed in the first test. Then the prepared sample is added as before, together with some starch indicator, and the excess sulfur dioxide is titrated with 0.1 *N* iodine until a blue color appears which is stable for a few seconds.

Free Sulfur Dioxide

The prepared liquor is pipetted into an Erlenmeyer flask, diluted, and titrated with 0.1 *N* sodium hydroxide, using phenolphthalein as an indicator. A pink color should be obtained which is stable for 60 seconds.

$$1 \text{ ml. } 0.1 \text{ } N \text{ NaOH} = 0.0032 \text{ g. } SO_2$$

Combined Sulfur Dioxide

The difference between the total sulfur dioxide and the free sulfur dioxide (as determined above) expressed in grams per 100 ml. gives the combined sulfur dioxide.

It is frequently desirable to make analyses on spent acid at the end of a cook or during the progress of the cook. Such analyses are more difficult to make than those made on fresh cooking acid because of the lignin compounds and organic acids which are present, and hence different analytical methods are required. The Palmrose iodate method²⁶ is suitable for analyzing spent sulfite liquor. It is carried out in three titrations, as follows:

Titration A

The sample is prepared by introducing 75 cc. of distilled water into a 250-cc. Erlenmeyer flask, followed by 2 to 4 drops of methyl red indicator and 2 cc. of starch-potassium iodide indicator. (The solution should be orange or yellow, a red color indicating the presence of acid in the water or the indicator.) Then 10 cc. of the prepared liquor sample (prepared as noted under method for sulfite digestion liquor) are introduced into the flask and titrated with 0.1 *N* potassium iodate solution. The flask should not be shaken until after the end point color begins to appear. The potassium iodate solution is conveniently prepared by dissolving 3.6 g. of potassium iodate in 1 l. of distilled

²⁶ G. V. Palmrose, *Tech. Assoc. Papers* 18: 309-310 (1935)

water. This is standardized against 0.1 *N* sodium thiosulfate by pipetting 25 cc. of the potassium iodate solution into a flask containing 100 cc. of distilled water, adding an excess of KI and about 5 cc. of 1.0 *N* sulfuric acid, and titrating the liberated iodine with the 0.1 *N* sodium thiosulfate solution.

1 cc. 0.1 *N* potassium iodate = 0.0032 g. of total sulfur dioxide

Titration B

The contents of the above flask are next titrated with 0.1 *N* sodium hydroxide to an orange or yellow end point. If the sample contains no lignin derivatives, a drop of 0.1 *N* sodium thiosulfate may be added to decolorize the starch before titrating with sodium hydroxide, but this step is eliminated if lignin derivatives are present.

1 cc. of 0.1 *N* sodium hydroxide = 0.0032 g. of apparent free sulfur dioxide

Titration C

If the sample contains lignin derivatives, 2.0 cc. of approximately 1.0 *N* sulfuric acid are added and the sample again titrated with 0.1 *N* potassium iodate solution to an end point at which one drop turns the solution orange or yellow.

1 cc. of 0.1 *N* potassium iodate = 0.0016 g. of reversible sulfur dioxide which was included in the apparent free sulfur dioxide titration and must be deducted to obtain the true free sulfur dioxide.

Calculations are carried out as follows:

Free sulfur dioxide (corrected) = apparent free sulfur dioxide (from titration B) minus reversible sulfur dioxide (from titration C.)

Combined sulfur dioxide = total sulfur dioxide (from titration A) minus free sulfur dioxide (corrected).

In addition to the analytical methods described above, gravimetric procedures may be used for determining the amount of silica, iron oxide, alumina, calcium oxide, and magnesium oxide in sulfite cooking liquor.

There are three types of sulfite cooks, known as the easy bleaching, Ritter-Kellner, and Strong or Mitscherlich. The following gives an idea of the concentrations generally employed in the three processes.

	Easy bleaching	Ritter- Kellner	Strong or Mitscherlich pulp
Total sulfur dioxide, %	4.5-7.0	4.0-4.5	2.8-4.0
Free sulfur dioxide, %	3.5-5.0	2.7-3.5	1.7-2.7
Combined sulfur dioxide, %	1.0-1.5	1.0-1.3	1.0-1.3

Most mills in the United States use acids stronger than 4.5%, and except for obsolete European mills, no one uses strengths of less than 4.0%. In extreme cases, the free sulfur dioxide may be as high as 8 to 10%, or even higher. The combined in the raw acid is generally maintained slightly higher than that indicated above, i.e., 1.6 to 1.8%, to compensate for the dilution which occurs when the raw acid is fortified in the recovery tower.

It should be pointed out at this time that although liquor composition is extremely important in sulfite cooking, the original concentration of the

liquor is subject to change during cooking, depending upon the temperature schedule followed and the method of handling digester relief. It is usual practice to put into the digester two or three times as much chemical as required to complete the cook, the excess chemical being "relieved" from the digester after the cook progresses. Once the cook is under way, the liquor composition is dependent upon the schedule of digester operation. Thus, the composition of the liquor becomes a secondary variable during cooking, since the pressure in the digester determines the composition.

Penetration of Sulfite Cooking Acid

One of the important factors in sulfite cooking is proper packing of the chips in the digester. By ordinary gravity filling about 15 lb. of chips (at 40% moisture content) can be charged per cubic foot of digester space. Today, many mills use mechanical, steam, or air chip distributors which distribute the chips uniformly in the digester. These increase the amount of wood held by the digester up to about 18 lb. of chips per cubic foot and hence increase the daily production of the pulp mill by about 15 to 20%.²⁷ It is necessary to increase the acid strength, particularly the combined, when chip packers are used, but there is usually an over-all saving in steam and chemical.

The first objective in the sulfite cooking process is to obtain complete penetration of the cooking liquor into the wood, since the wood will be improperly cooked if the cooking liquor does not penetrate uniformly throughout the chips. Acid sulfite liquor penetrates with greater difficulty than alkaline cooking liquors. Penetration is so important in the sulfite process that it is common to regard the cooking process as taking place in two stages, the penetration stage, and the actual cooking stage. As a rule, cooking is started before penetration is complete. Incomplete penetration of cooking liquor results in high screenings, low yield of screened pulp, and high bleach requirement of the pulp, and high dirt content due to brown slivers.

When the chips first contact the cooking liquor, they increase in size. Swelling is practically negligible in the lengthwise direction, but is considerable in the radial and tangential directions (slightly greater in the latter). The cooking liquor penetrates into the lumen or central cavity of the fiber and then diffuses into the fiber wall to come into contact with the ligneous substance. This occurs almost immediately with those fibers on the outside of the chips, but appreciable time is required for the liquor to reach the center of the chip. In the case of sulfite liquor, the transmission of liquor through the chips takes place much more rapidly (about 100 times) in a

²⁷ A. Christensen, *Pulp Paper Mag. Canada* 48, No. 3: 110-114, Convention Issue (1947)

longitudinal direction than in a transverse direction, the liquor passing from tracheid to tracheid by means of the bordered pits, and from tracheid to ray cells by means of the simple pits.

Two types of penetration are to be considered in the penetration of wood by sulfite cooking liquor: (1) flow of liquid under pressure and (2) natural diffusion of solute. Flow of liquid occurs with menisci present, whereas diffusion takes place through a liquid-saturated medium. Flow of liquid is dependent upon capillarity and applied pressure. Diffusion is a direct function of void volume and differs from flow of fluids in that it is dependent only on the effective capillary cross section, and not on the actual size of the capillaries.²⁸ The rate of fluid flow is about 50 to 100 times greater in the longitudinal direction than in either the radial or tangential directions,^{29, 30} but according to Stamm, the ratio of longitudinal to transverse diffusion of solute is only about 10 to 12. Permeability of wood to fluid flow in both the longitudinal and transverse directions is determined by the size of the pit-membrane pores that connect the fibers.^{28, 31, 32}

When dry wood is used, the rate of filling of the chips with liquor and the rate of solution and diffusion of air are important factors.³³ If the wood is completely saturated with water, penetration takes place entirely by diffusion of solute. Most rapid penetration occurs when the wood is green and moist, that is, when the moisture content is 35 to 40% of the wet wood weight. The sulfite process can, however, handle wood having wide differences in moisture without detriment to pulp quality, provided that wet and dry wood are not used in the same digester. Wood which has been stored too long in water is very resistant to penetration because of excessive water in the cell walls and lumen.

Under most circumstances, complete filling of the chips with sulfite liquor probably occurs fairly early in the cooking cycle, particularly if high hydrostatic pressure is applied early in the cook. However, complete diffusion of the combined sulfur dioxide into the chip may not occur until sometime later, because the free sulfur dioxide in the liquor diffuses as much as four times faster than the combined.^{34, 35} If enough time is not allowed for the combined to reach the center of the chips, discoloration oc-

²⁸ A. J. Stamm, *Tappi* 32, No. 5: 193-199 (May, 1949)

²⁹ H. W. Johnston and O. Maass, *Can. J. Research* 3: 140 (1930)

³⁰ J. H. Sutherland, H. W. Johnston and O. Maass, *Can. J. Research* 10, No. 1: 36-72 (Jan., 1934)

³¹ A. J. Stamm, *J. Agr. Research* 38: 23 (1929)

³² A. J. Stamm, *U. S. Dept. Agr. Tech. Bull.* 927 (1946)

³³ F. H. Yorston, Pulp Paper Research Institute of Canada, Lab. Report No. 23 (1943)

³⁴ R. de Montigny, *Pulp Paper Mag. Canada* 34, No. 2: 109-110 (Feb., 1932)

³⁵ R. de Montigny and O. Maass, *Dominion Forest Service Bull.* 87, Canadian Dept. of Interior, Ottawa (1935)

curs on the inside of the chips during cooking, resulting in a condition known as "red chips," or "burning." This occurs if the delignification temperature is reached before the combined penetrates the chip, because under these conditions lignosulfonic acid tends to resinify. A high concentration of sulfur dioxide in the cooking liquor has a beneficial effect on overall penetration, particularly in the range of lower concentrations.³⁶ A rough idea of the relative extent of penetration of the free and combined portions of the cooking liquor into the chips can be obtained by staining a section of the chips with indicators, using brom phenol blue for measuring the extent of penetration of the free sulfur dioxide, and either methyl orange or brom thymol blue for measuring the extent of penetration of the combined sulfur dioxide.

The size and the shape of the chips has an important effect on the penetration of sulfite cooking liquor. McGovern and Chidester³⁷ measured the penetration of sulfite cooking liquor into chips of different lengths and found that increasing the chip length from $\frac{1}{4}$ in. to $1\frac{1}{8}$ in. resulted in an increase in the time of penetration from 15 minutes to 270 minutes at 110° C. The length of the chips used commercially ordinarily varies from about $\frac{1}{2}$ to $\frac{3}{4}$ in. for easy bleaching pulp, and from $1\frac{1}{4}$ to $1\frac{3}{4}$ in. for strong unbleached pulps of the Mitscherlich type. Conventional spruce chips require from $1\frac{1}{2}$ to 2 hours for penetration, and hemlock chips a slightly longer time. Hägglund³⁸ found that the length of the chips, within reasonable limits, had little effect on the rate of delignification, which he attributed to the cooking acid diffusing into the chips and the lignosulfonic acid passing out of the chips in a radial or tangential direction. Morgan and Dixon³⁹ found that increasing chip length from $\frac{1}{2}$ to $1\frac{1}{4}$ in. results in poor delignification, even when the time taken to reach 110° C. was greatly extended. The use of high initial pressure greatly improved the results, e.g., within the normal chip range ($\frac{1}{2}$ to $\frac{3}{4}$ in.), a difference was obtained of less than 1 permanganate number between the center and end sections of the chip when the cook was carried out at high initial pressure, compared with a difference of 1 to 2.0 for cooks carried out in the normal manner (maximum temperature 140° C., maximum pressure 85 p.s.i.).

Increasing the temperature of the liquor increases the rate of penetration, but, as mentioned above, the temperature must not exceed the critical point (110 to 120° C.) until penetration of the combined is complete. Han-

³⁶ J. N. McGovern, *Paper Trade J.* 103, No. 20: 297-310 (Nov. 12, 1936)

³⁷ J. N. McGovern and G. H. Chidester, *Paper Trade J.* 99, No. 18: 227-232 (May 3, 1934)

³⁸ E. Hägglund, *Svensk Papperstidn.* 39, No. 6: 95-100 (Mar. 31, 1936) through B. L. Grondal, *Paper Mill* 62, No. 34: 14-20 (Aug. 26, 1939)

³⁹ H. Morgan and H. P. Dixon, *Paper Trade J.* 107, No. 7: 72-74 (Aug. 18, 1938)

sen and Hazelquist⁴⁰ found that the rate of penetration of both the combined and the free sulfur dioxide in sulfite cooking liquor increases in a straight-line relationship with temperature in the range between 20 to 70° C. McGovern⁴¹ found that for each 10° C. rise in temperature, the penetration time was reduced by one-half hour in the range 100 to 120° C.

Preliminary penetration of the chips by sulfite liquor and forced penetration of sulfite cooking liquor into the chips by hydrostatic pressure are some of the methods which have been suggested for shortening the cooking cycle and producing a more uniform pulp. Presteaming of the wood before admission of the cooking liquor has long been recognized as an aid to penetration. Presteaming is extensively practiced in the Mitscherlich process.⁴² The use of steam in this way drives out the air and heats up the wood so that when the relatively cool liquor is added, a partial vacuum is formed which sucks the liquor into the wood. Presteaming is most effective with wet wood.⁴³

Since air is known to interfere with penetration, air evacuation of the digester preliminary to the addition of the liquor has been suggested.^{43,44} Evacuation is not practical in lined digesters because of the tendency for the lining to break off. Furthermore, there is no over-all reduction in cooking time. De Montigny and Maass⁴⁴ found that a preliminary pretreatment of the chips with sulfur dioxide, followed by the application of hydrostatic pressure, permitted heating of the digester to 140° C. in a very short time (½ hour) without the production of "burnt" centers.

The introduction of hot cooking liquor (70 to 85° C.) increases the rate of penetration of the chips. In mills using the hot acid system (chemipulp system), hot liquor from a high-pressure accumulator is pumped to the digester through a blow-off fitting. The digester is vented at the top until the air is removed, and then the vent is closed. Liquor is added until the digester is full, and after the vent is closed, liquor is pumped from the accumulator into the digester until a hydrostatic pressure of about 40 to 45 p.s.i. is built up. Then the top and side relief valves are opened and liquor is precirculated from the accumulator through the digester for 15 to 120 minutes. This circulation produces a more uniform penetration of the chips and equalizes the temperature in the digester.⁴⁵⁻⁴⁷ At the end of the

⁴⁰ R. B. Hansen and S. Hazelquist, *Paper Trade J.* 95, No. 20: 225-227 (Nov. 17, 1932)

⁴¹ J. N. McGovern, *Paper Trade J.* 103, No. 20: 297-310 (Nov. 12, 1936)

⁴² C. R. Bergson, *Svensk Papperstidn.* 39, No. 3: 32-36 (Feb. 15, 1936)

⁴³ E. Hägglund, T. Bergek, G. Carlsson and B. Wadmann, *Svensk Papperstidn.* 43, No. 6: 99 (Mar. 31, 1940)

⁴⁴ R. de Montigny and O. Maass, *Dominion Forest Service Bull.* 87, Canadian Dept. of Interior, Ottawa (1935)

⁴⁵ O. Kreissler, *Svensk Papperstidn.* 38, No. 19: 630, 635-636, 638 (Oct. 15, 1935)

⁴⁶ T. Samson, *Svensk Papperstidn.* 39, No. 1: 3-6 (Jan. 15, 1936)

⁴⁷ G. Soltau, *Svensk Papperstidn.* 39, No. 11: 202-203 (June 15, 1936)

circulating period, the liquor pump is stopped and excess acid in the digester is forced out by the hydrostatic and gas pressure in the digester. The cook is then ready to begin, starting at what is the equivalent of the second hour in a normal cook. Because the cook is started at a high initial temperature, steam condensation and acid dilution are held to a minimum. This procedure also has the effect of minimizing the dilution of combined which normally occurs when the digester is heated up to temperature from cold acid. The pulp has fewer screenings and is produced in greater yield than is obtained by ordinary methods.

Sapwood is much more permeable to sulfite cooking acid than heartwood. Maass and coworkers^{48, 49} have shown that the rate of flow of liquid (water) through sapwood may be 200 times that through heartwood. Stamm⁵⁰ found, using a capillary rise method, that the average pit membrane pore radius is from 0.18 to about 11.0 microns in sapwood, and about 0.05 to 5.0 microns in heartwood, which explains the greater difficulty in penetrating heartwood. Summerwood fibers require a longer penetration period than springwood fibers because of their thicker walls. In certain species, e.g., the pines, resin ducts filled with resins have been found to be a cause of poor penetration.⁵¹ In the hardwoods, tyloses may cause poor penetration. Certain species of the pines and Douglas fir cannot be pulped satisfactorily by the sulfite process because of specific chemicals located in the heartwood unless special cooking conditions are used.

Variables in Sulfite Pulping

The principal variables in sulfite pulping for a given digester charge are temperature of cooking, free sulfur dioxide present, total sulfur dioxide present, combined sulfur dioxide present, liquor ratio, and time of cooking. These are discussed in the following sections. It should be kept in mind that most of the investigations reported in the literature on pulping have been carried out in laboratory digesters under ideal conditions of uniform liquor circulation and uniform temperature and chemical composition. This is quite different from the non-uniform conditions which exist in mill digesters, and hence the results of laboratory work must be applied with caution in predicting results to be obtained in commercial operation.

Effect of Temperature in Sulfite Process

The reactions which take place during sulfite pulping are heterogeneous and not well understood. The active constituents of the liquor are calcium

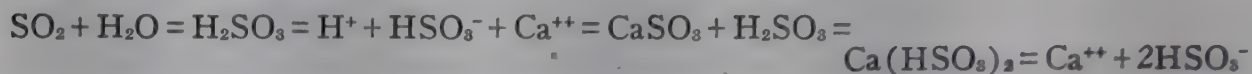
⁴⁸ H. W. Johnston and O. Maass, *Can. J. Research* B140 (1930)

⁴⁹ J. H. Sutherland, H. W. Johnston and O. Maass, *Can. J. Research* 10: 36 (1934)

⁵⁰ A. J. Stamm, *J. Phys. Chem.* 36: 312 (1932)

⁵¹ W. B. Beazley, H. W. Johnston and O. Maass, *Dominion Forest Service Bull.* 95, Canadian Dept. of Mines and Resources, Ottawa (1939)

ion, hydrogen ion, bisulfite ion, and sulfur dioxide. Sulfur dioxide is present in both the gaseous and the dissolved state and is in equilibrium with sulfurous acid solution and calcium bisulfite solution, according to the following relationship:



Any increase in the temperature of the system affects the equilibrium ratio by shifting the equilibrium to the left and decreasing the concentration of bisulfite ions. Table III, taken from work by Maass and coworkers,⁵¹ shows the effect of temperature on the amount of free sulfur dioxide in solution. If the temperature becomes too high, so much sulfur dioxide is removed from solution that part of the base precipitates (although there is a tendency to form a supersaturated solution). This is the cause of digesters "liming up."

TABLE III

EFFECT OF TEMPERATURE AND TOTAL SULFUR DIOXIDE ON THE AMOUNT OF SULFUR DIOXIDE AS SUCH IN SOLUTION

Per cent total SO ₂	Per cent of total SO ₂ present as SO ₂	
	18° C.	25° C.
2	31.3	36.6
4	35.2	40.2
6	37.0	42.9
8	38.4	43.2

In the early stages of cooking, temperature in the digester must be brought up slowly so that the liquor may penetrate the chips evenly. Acid penetrates the chips more rapidly as the temperature is increased, but the chips must be thoroughly saturated with acid before the critical temperature is reached (110 to 120° C.), since otherwise the chips will be "burnt." Slow temperature rise in the early stages of cooking reduces the danger of burning the cook, inhibits the precipitation of combined in the liquor, increases the yield, and improves the strength of the pulp. The time taken to reach maximum temperature can be shortened if acids of high free sulfur dioxide are used.

During the pulping period, i.e., after the initial penetration period, maximum temperature is the most important pulping variable, and it is the only reliable means of controlling the progress of the cook. The maximum temperature used in the sulfite process ordinarily falls in the range of 130 to 150° C. (the digester pressure being in the range of 60 to 80 p.s.i.). Swanson⁵² gives 150° C. as the top maximum temperature which should be

⁵² W. H. Swanson, *Chemistry of the Sulfite Process*, pp. 113-116. Lockwood Trade J. Co., New York, N. Y. (1928)

used for a digester pressure of 75 p.s.i., inasmuch as the free sulfur dioxide content is greatly reduced at higher temperatures. De Montigny and Maass⁵³ report a temperature of 140° C. as the most practical cooking temperature, since cooking at a lower temperature increases the time of cooking, whereas cooking at a higher temperature does not appreciably reduce the cooking time, but does reduce the yield and strength of pulp. Temperatures in the range of 150° C. are used when making high alpha pulps. In the Mitscherlich process, the temperature is usually about 118 to 130° C., and the pressure from 45 to 75 p.s.i. The maximum temperature depends somewhat upon the species of wood; hemlock requires about a 10° higher temperature than spruce. The temperature schedules found best by Swanson⁵² when pulping spruce in the laboratory for different grades of pulp are given in Table IV. These are not commercial cooking schedules, but rather are illustrations of schedules which produce very high-quality pulps.

TABLE IV
COOKING SCHEDULES FOR DIFFERENT GRADES OF SULFITE PULP

	Penetration period	Pulping period	Total time
Sulfite pulp for news	2 hours to 110° C.	6.5 hours from 110–150° C. at uniform rate of 6° C./hour	8.5 hours
Strong sulfite pulp	2 hours to 110° C.	8 hours from 110–145° C. at uniform rate of 4.5° C./hour	10 hours
Easy-bleaching sulfite pulp	2 hours to 110° C.	7 hours from 110–145° C. at uniform rate of 5° C./hour. Holding 1.5 hours at 145° C.	10.5 hours
Strong very easy-bleaching sulfite pulp	2 hours to 110° C.	1 hour from 110–120° C. 9 hours from 120–140° C. at uniform rate of 2.2° C./hour	12 hours

There is no critical temperature below which delignification does not occur.⁵⁴ There is some cooking when chips are soaked in sulfite acid at 80° C. However, high temperatures are necessary when making bleachable pulps and are required with all pulps in order to complete the cooking in a reasonable period of time. The empirical rule used so widely in kinetics which states that the rate of reaction is approximately doubled for each 10° C. rise in temperature is fairly applicable to sulfite cooking. Miller and Swanson⁵⁵ found that the time for lignin removal is reduced by one-half for each 10° C. rise in temperature between 120 to 150° C.

⁵³ R. de Montigny and O. Maass, *Dominion Forest Service Bull.* 87, Canadian Dept. of Interior, Ottawa (1935)

⁵⁴ F. H. Yorston, *Dominion Forest Service Bull.* 97, Canadian Dept. of Mines and Resources, Ottawa (1942)

⁵⁵ R. N. Miller and W. H. Swanson, *Paper Trade J.* 78, No. 15: 178–181 (Apr. 10, 1924)

Increasing the temperature not only increases the rate of delignification but also increases the rate of removal of cellulose and hemicellulose. The use of too high a temperature lowers the yield, about 0.5% for each 10° C. rise in the commercial range, and is very injurious to papermaking properties because it removes too much hemicellulose and degrades the cellulose. Temperature appears to be a more critical factor in determining the chain length of the cellulose in sulfite pulp than either the composition of the cooking liquor or the time of cooking.⁵⁶ The effect of temperature on the loss in carbohydrate material during sulfite cooking expressed as yield at 95% of delignification is shown in Figure IV-4.⁵⁷ Apparently very little sugar is

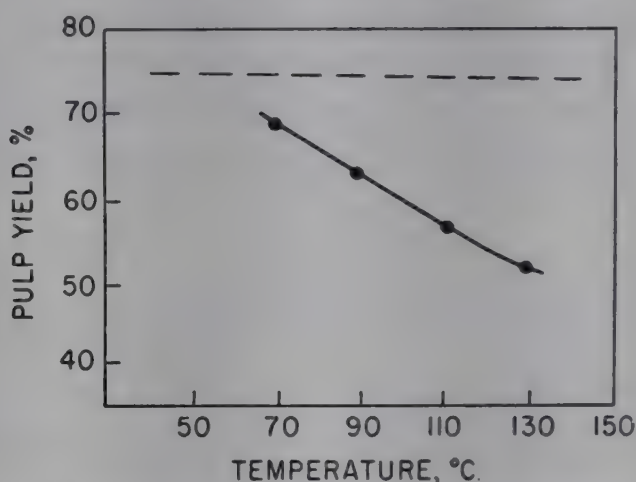


Fig. IV-4. Effect of temperature on actual (—) and calculated (--) yield of pulp from spruce cooked by sulfite process to 95% of delignification.

formed in the digester by hydrolysis of the true cellulose until the temperature is raised over 100° C.,⁵⁸ but temperatures over 140° C. have a highly degrading effect on cellulose.⁵⁹ Relatively low temperatures are used when "strong" pulps are desired, and relative high temperatures are used where "free" pulps are desired. One reason that Mitscherlich pulp is so much stronger than ordinary sulfite pulp is the lower temperatures which are used.

In general, it may be stated that the lowest temperature which gives a satisfactory degree of purity in a reasonable time is the best temperature to use. Low maximum cooking temperature results in a pulp of high yield, low screenings, and high strength.⁶⁰ The effects of cooking temperature on yield, permanganate number, and bursting strength of pulp ob-

⁵⁶ F. Wuntz, *Papier-Fabr. Wochbl. Papierfabr. No. 4*: 128-131 through *B.I.P.C. 15*: 261

⁵⁷ J. M. Calhoun, F. H. Yorston and O. Maass, *Can. J. Research 17B*, No. 4: 125 (Apr., 1939)

⁵⁸ E. C. Sherrard and C. F. Suhm, *Ind. Eng. Chem. 14*: 931 (1922) and *17*: 194 (1925)

⁵⁹ R. N. Miller, *Paper Trade J. 81*, No. 23: 55 (1925)

⁶⁰ J. N. McGovern, *Paper Trade J. 103*, No. 20: 297-310 (Nov. 12, 1936)

tained from black spruce are shown in Figure IV-5.⁶¹ These data were obtained by cooking the wood for 10 hours at a liquor ratio of 4.3 cc./g., using no top relief; the liquor composition was 6.2% total, 5.0% free, and 1.2% combined. Anderson⁶² obtained a consistent improvement in pulp strength and a reduction in screenings by reducing the maximum cooking temperature from 153 to 133° C.

In commercial practice, production requirements fix the maximum allowable cooking temperature. The demands of production, plus the strength of available acid (limiting digester pressure) and specified bleach-

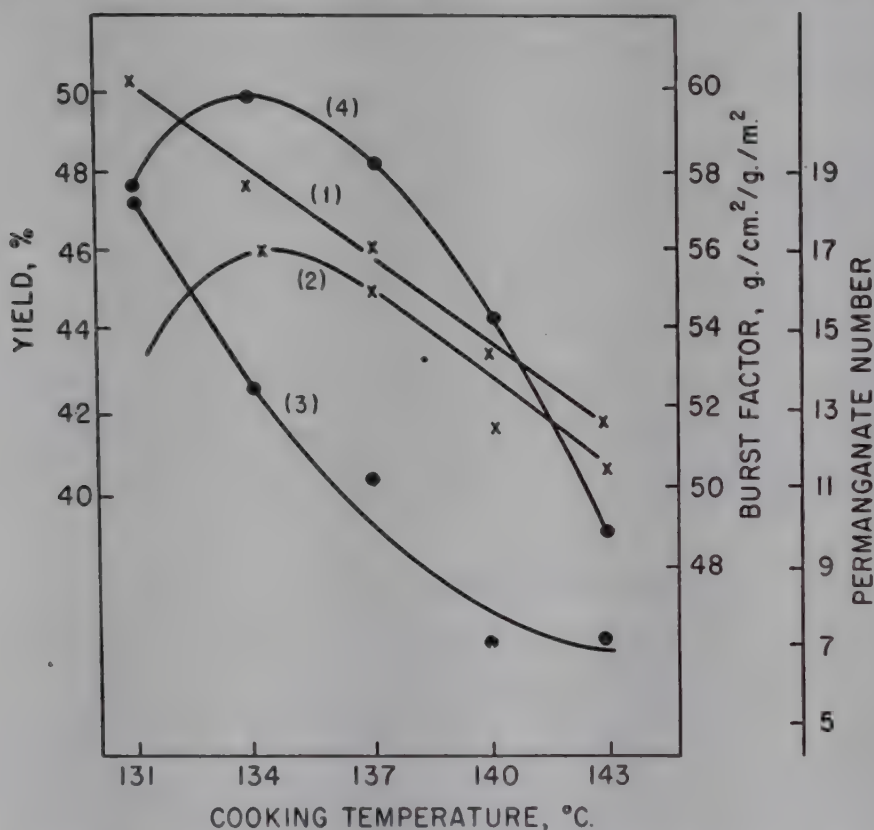


Fig. IV-5. Effect of cooking temperature in sulfite process on total yield (1), screened yield (2), permanganate number (3), and bursting strength (4) of pulp.

ability requirements largely determine the cooking temperature which must be used.⁶³ Modern practice in making easy bleaching pulp is toward high acid concentration and high pressure in order to retain a high concentration of sulfur dioxide in solution and permit pulping at the lowest possible temperature in an allowable cooking time. The combination of high pressure, low maximum temperature, and strong cooking acid is beneficial from the standpoint of yield and strength of pulp produced.

⁶¹ E. Ott, ed., *Cellulose and Cellulose Derivatives*, p. 500. Interscience Publishers, Inc., New York, N. Y. (1943)

⁶² O. E. Anderson, *Tech. Assoc. Papers* 18: 252-254 (June, 1935)

⁶³ T. R. Moore and F. H. Yorston, *Pulp Paper Mag. Canada* 47: 113-115, Convention Issue (1946)

The method of heating the digester varies with the process. In the Mitscherlich process, cooking is done by steam coils, the chips generally being steamed with direct steam before the liquor is added in order to improve penetration. In the Ritter-Kellner process, steam is injected directly into the cooking liquor by blowing directly into the digester or by admitting through a tee or injector in a liquor-circulating line. In the Morterud process, indirect heating and forced circulation are used. Indirect heating of the cooking liquor with forced circulation through the digester is becoming increasingly popular, since this permits better control of cooking conditions, eliminates "zoning" in the digester, and permits more accurate instrumentation. Better yields, gains in pulp strength, cleanliness, more uniform pulp, lower steam consumption, and shorter cooking times are obtained.^{64, 65} Indirect heating is essential if an acid recovery system is to be used in order to prevent dilution of the liquor. There are several methods of circulating the liquor: the liquor may be taken from the bottom of the digester, passed through a heat exchanger, and returned into the top of the digester, or it may be taken from a point near the middle of the digester, pumped through a heat exchanger, and then returned in two lines, one entering the bottom of the digester and the other at the top. Forced circulation of the liquor is highly desirable when chip packers are used.

Effect of Pressure in Sulfite Process

The pressure developed in the digester during sulfite cooking is due to the steam pressure plus the pressure of sulfur dioxide gas. Thus, changing the pressure not only affects the temperature of cooking but also changes the partial pressure of sulfur dioxide in the digester which, in turn, affects the composition of the cooking liquor. The control of temperature and pressure fixes the concentration of sulfur dioxide in the cooking liquor.

There is an upper permissible pressure limit for sulfite cooking which depends upon the strength of the digester. At present, it is not practical to construct digesters capable of withstanding the full pressures developed during cooking, and hence the pressure must be relieved either at intervals or continuously during cooking to obtain the desired temperature without exceeding a safe operating pressure. As mentioned previously, the digester is normally charged with two to three times as much chemical as required to complete the cook, the high initial concentration of chemical being desirable from the standpoints of promoting the penetration of cooking liquor into the chips and in securing a high reaction rate. This excess chemical

⁶⁴ N. Bernheimer, *Pulp Paper Mag. Canada* 47, No. 11: 99-102 (Oct., 1946)

⁶⁵ T. A. Pascoe and M. Fraser, *Paper Trade J.* 112, No. 12: 143-148 (Mar. 20, 1941)

must be relieved long before the digester is up to maximum temperatures. Relieving the digester to a constant pressure during the period of rising temperature lowers the concentration of sulfur dioxide in solution.

Most sulfite digesters have a limiting pressure not in excess of 70 to 80 p.s.i. However, with the trend toward stronger cooking liquors, there has been a tendency to use higher pressures, and some sulfite mills are now operating at pressures as high as 90 to 100 p.s.i. with strong acid. There is no benefit in using cooking liquors of higher than normal concentrations unless the digester pressure is high enough to keep the additional sulfur dioxide in solution. For example, if the digester pressure must be limited to about 95 lb., no advantage will be gained in going to acid concentrations higher than about 6.5% free sulfur dioxide,⁶⁶ except for improved penetration in the early stages of cooking.

Toward the end of the cooking cycle, it is advantageous to lower the pressure in the digester gradually about 15 to 20 p.s.i. in order to minimize attack on the cellulose, which in turn increases the yield of pulp obtained. At the end of the cook, the pressure in the digester is relieved down as low as possible to prevent the breaking up of shives and to obtain the maximum recovery of sulfur dioxide. The remaining pressure (about 15–40 p.s.i.) should be sufficient to empty the digester when the digester is “blown.” The recovery of relief gas and relief liquor has already been discussed.

Effect of Total Sulfur Dioxide in Sulfite Process

A typical sulfite cooking acid generally contains about 6% total sulfur dioxide, but the trend in recent years has been toward the use of higher acid concentrations. A total sulfur dioxide content of 7 to 8% is not uncommon today, and some mills use an extreme of 10%. An acid containing 6% total sulfur dioxide used at the normal liquor-to-wood ratio of 4.5 to 1 would mean that 27.0% total sulfur dioxide was initially charged on the weight of oven-dry wood.

Strong acid permits faster cooking and a lower maximum cooking temperature which, in turn, results in a high yield and a strong pulp, although low tearing and folding strengths have been reported for high acid concentrations on some species.^{67,68} McGovern⁶⁹ found that increasing the total sulfur dioxide concentration from 5 to 20% reduced the digestion time from 9 hours to 5½ hours when the digestion was carried out at a constant temperature of 140° C. The relation between total sulfur dioxide content and the temperature required to obtain pulp of equivalent quality in a total time of 9 hours is shown in Figure IV-6, taken from work of McGovern.⁶⁹

⁶⁶ W. F. Holzer, *Paper Trade J.* 110, No. 16: 35–39 (Apr. 20, 1944)

⁶⁷ A. H. Lundberg, *Paper Trade J.* 92, No. 20: 53–54 (May 14, 1931)

⁶⁸ A. Sander, *Paper Trade J.* 81, No. 10: 50–52 (Sept. 2, 1920)

⁶⁹ J. N. McGovern, *Paper Trade J.* 103, No. 20: 297–310 (Nov. 12, 1936)

The greatest reduction in temperature required was obtained in the range of 5% total sulfur dioxide and higher. Stronger acids are required the wetter the wood because of the dilution by the extra water in the chips.

The results of Simerl,⁷⁰ based on a 10-hour cook of black spruce, showed that the total sulfur dioxide decreased fairly progressively from 6.0% at the beginning of the cook to about 0.5% at the end of the cook. The decrease in sulfur dioxide is attributed to relief and to consumption of chemical by the wood.

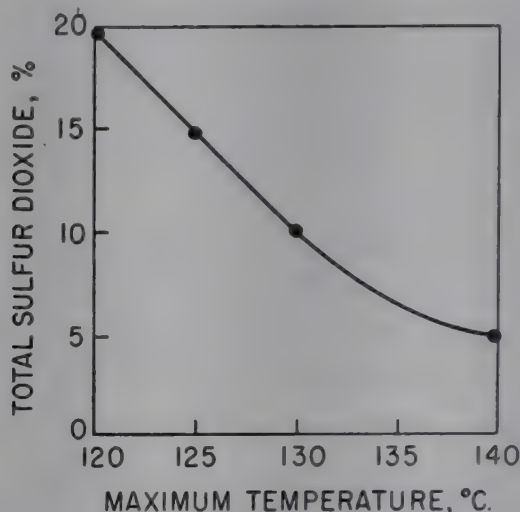


Fig. IV-6. Relationship between total sulfur dioxide content and maximum temperature required in sulfite pulping to obtain pulp of equivalent quality at constant time of cooking (9 hours).

Effect of Free Sulfur Dioxide in Sulfite Process

The amount of free sulfur dioxide in commercial sulfite cooking acid is dependent upon the pressure-temperature schedule followed during the cooking cycle. Once the digester has been brought up to pressure and relief started, the amount of free sulfur dioxide in the liquor becomes a function of temperature. Koon⁷¹ found, in the case of sulfite cooks carried without relief (which is not the practice in commercial cooking), that the concentration of free sulfur dioxide remained relatively constant during the period of the cook until the digester was blown at the end of the cook. This is in agreement with the theory of sulfite pulping, since it is only the amount of sulfur dioxide equivalent to that theoretically combined in the form of bisulfite [$\text{Ca}(\text{HSO}_3)_2$] which permanently enters into the sulfonation reaction (see formula on page 107). The "true" or "excess" free sulfur dioxide (free minus the combined), or sulfur dioxide in excess of that theoretically required to form bisulfite, would therefore be expected to remain constant throughout the cook if there were no relief. In commercial operation where

⁷⁰ L. Simerl, *Tech. Assoc. Papers* 23: 114 (June, 1940)

⁷¹ E. Ott, ed., *Cellulose and Cellulose Derivatives*, p. 496. Interscience Publishers, Inc., New York, N. Y. (1943)

the digester is relieved to constant pressure, the free sulfur dioxide content of the cooking liquor decreases considerably during the period of the cook.⁷²⁻⁷⁴ However, the "true" or "excess" free sulfur dioxide remains relatively constant after 6 hours of cooking, regardless of the initial concentration of the cooking acid.^{74, 75} This is as would be expected, since in a system where pressure and volume of digester contents are fixed, there can be but one concentration of excess sulfur dioxide for a given temperature.

The free sulfur dioxide in the cooking liquor is the active cooking agent, and ordinarily between 80 to 85% of the total sulfur dioxide should be present in this form. The initial charge of a typical sulfite cooking acid contains about 4.8% free sulfur dioxide, or about 21.6% on the weight of the oven-dry wood at the normal liquor-to-wood ratio of 4.5 to 1. Sulfite liquor must contain a minimum concentration of free sulfur dioxide in order for cooking to take place. Richter⁷⁶ has shown that heating of wood at a temperature of about 100° C. in weak sulfur dioxide solutions (1% solution) promotes a conversion of lignin to an inert form. Under these conditions, the weak sulfur dioxide functions primarily as an acid rather than as a sulfonating agent. Wood treated in this way cannot be readily delignified, even if subsequently treated with stronger liquor, on account of the insolubilizing effect of the acid on the lignin.⁷⁷

De Montigny and Maass⁷⁸ showed that increasing the free sulfur dioxide in the range of 2.5 to 6.4 decidedly increased the rate of reaction when the time and temperature were held constant and the pressure maintained at a point to preclude relief. Maass and coworkers^{79, 80} showed that the rate of delignification is directly related to the concentration of free sulfur dioxide in the liquor. As would be expected, increasing the percentage of free sulfur dioxide in the cooking acid allows a considerable reduction in the cooking temperature for a given cooking time. De Montigny and Maass⁸¹ obtained better results by cooking for a short time at high free sul-

⁷² E. Ott, ed., *Cellulose and Cellulose Derivatives*, p. 497

⁷³ A. Kung and B. Sieber, *Svensk Papperstidn.* 49, No. 1: 145-147 (Apr. 15, 1945)

⁷⁴ R. N. Miller and W. H. Swanson, *Chemistry of the Sulfite Process*, p. 52. Lockwood Trade J. Co., New York, N. Y. (1928)

⁷⁵ E. Ott, ed., *Cellulose and Cellulose Derivatives*. Interscience Publishers, Inc., New York, N. Y. (1943)

⁷⁶ G. A. Richter, *Tappi* 32, No. 12: 553-559 (Dec., 1949)

⁷⁷ R. N. Miller, W. H. Swanson and R. Soderquist, *Chemistry of the Sulfite Process*, pp. 80-91. Lockwood Trade J., New York, N. Y. (1928)

⁷⁸ R. de Montigny and O. Maass, *Dominion Forest Service Bull.* 87, Canadian Dept. of Interior, Ottawa (1935)

⁷⁹ J. M. Calhoun, F. H. Yorston and O. Maass, *Can. J. Research* 15B: 457 (1937)

⁸⁰ F. H. Yorston, *Dominion Forest Service Bull.* 97, Canadian Dept. of Mines and Resources, Ottawa (1942)

⁸¹ R. de Montigny and O. Maass, *Dominion Forest Service Bull.* 87, Canadian Dept. of Interior, Ottawa (1935)

fur dioxide concentration than by cooking for a longer time at a lower concentration when the temperature was held constant at 140° C. They found, under these conditions, that the lignin content approached a minimum and bursting strength approached a maximum as the free sulfur dioxide content of the liquor was increased up to 5 to 6%. The yield approached a minimum, but further work showed that yield was independent of the concentration of free sulfur dioxide in the cooking acid when pulp of given lignin content was produced.⁸² Using a fairly weak acid (5.5% total SO₂) and a constant maximum cooking temperature of 138° C., Miller and Swanson^{83, 84} found that differences in liquor concentration resulting from variation in digester pressure between 65 to 80 p.s.i. had little or no effect on the yield and strength of the pulp, although there was a slight decrease in yield and strength at a pressure of 100 p.s.i.

The free sulfur dioxide content must be maintained above a minimum value of 0.1% at all times for liquor ratios normally used in order to prevent the reversion of soluble calcium bisulfite to insoluble calcium monosulfite, and to prevent "blackening" of the pulp.⁸⁵ If the free sulfur dioxide becomes lower than this minimum, such as might occur near the end of the cook when the digester is being relieved, darkening may occur, due to splitting off of the loosely held sulfur dioxide from the dissolved wood substance.

Effect of Combined Sulfur Dioxide in Sulfite Process

The initial charge of a typical sulfite cooking acid contains about 1.2% combined sulfur dioxide, or about 5.4% on the oven-dry weight of the wood at the normal liquor-to-wood ratio of 4.5 to 1. The amount of combined in sulfite liquor is definitely established by the amount of calcium hydroxide and water in the cooking liquor and by the solubility of calcium bisulfite. (Beyond a certain point, addition of lime brings about no further increase in combined.) The amount of combined in the liquor indirectly controls the free sulfur dioxide content so long as the total sulfur dioxide content remains the same.

As already indicated, the main mechanism of sulfite pulping is one of sulfonation brought about by the action of free sulfur dioxide. The combined plays no role in this reaction, its principal function being to prevent the polymerization of the strong lignosulfonic acids into insoluble dark-colored products. If lignosulfonic acids are heated above a temperature of

⁸² J. M. Calhoun, F. H. Yorston and O. Maass, *Can. J. Research* 15B: 457 (1937); 17B: 121 (1939)

⁸³ R. N. Miller and W. H. Swanson, *Chemistry of the Sulfite Process*, pp. 64-66. Lockwood Trade J. Co., New York, N. Y. (1928)

⁸⁴ R. N. Miller and W. H. Swanson, *Paper Trade J.* 74, No. 16: 136 (Oct. 16, 1924)

⁸⁵ W. H. Birchard, *Paper Trade J.* 85, No. 12: 119-122 (Sept. 22, 1927)

about 100 to 110° C. in the absence of the base ion, dark-colored products are formed as a result of the above mentioned polymerization. The action of sulfur dioxide alone on lignin at temperatures over 100° C. leads to the formation of an insoluble product which will not dissolve.⁸⁶ The presence of the base ion prevents this from taking place during the cook at temperatures over 100° C., and hence, it is very important not to carry the cook beyond exhaustion of the combined. It is possible to cook with sulfur dioxide alone, but the cook would necessarily have to be carried out at temperatures below the range of 100 to 120° C. The presence of base in the liquor permits the cook to be carried out at higher temperatures and results in a pulp which is brighter and has a lower bleach requirement.

The combined by itself has no appreciable effect on the rate of delignification, which is generally believed to be controlled by the rate of sulfonation. Thus, if the free sulfur dioxide is maintained constant, varying the combined within reasonable limits should have no effect on the rate of delignification. However, if the total sulfur dioxide is maintained constant, increasing the combined would be expected to reduce the rate of delignification by virtue of the reduced free sulfur dioxide which results. Very high combined (as is possible in the case of sodium-base liquors) increases the consumption of chemical and slows down the cooking reactions, although the latter can be compensated for by higher cooking temperature.⁸⁷

The pH of sulfite cooking liquor is around 2.0 at the start of the cook and drops to about 1.0 at the end. Sulfurous acid is virtually un-ionized at the temperatures existing during the cook so that the low pH at the end of the cook must be due principally to strong lignosulfonic acids and possibly to a lesser extent to sulfuric acid or other sulfur acids present in the liquor.⁸⁸ Because the combined sulfur dioxide counteracts the decrease in pH promoted by the formation of the lignosulfonic acids and organic acids produced during the cook, the hydrolyzing effect of the liquor on the carbohydrate fraction of the wood is minimized. As a result of this action, the yield and strength of the pulp are increased, although, as pointed out above, the rate of delignification may be decreased and the total cooking time increased. Chidester⁸⁹ obtained reduced yield with combined over 2.5 to 3.0% in the case of sodium-base liquor, but this was probably due to the elevated temperatures used to compensate for the decelerating effect of the base on the rate of delignification. Many chemists believe that the base ions are involved in base exchange reactions with the sulfonated wood.

⁸⁶ R. N. Miller, *Paper Trade J.* 81, No. 23: 55 (1925)

⁸⁷ C. R. Mitchell and F. H. Yorston, *Pulp Paper Mag. Canada* 37: 195-198, 209 (Mar., 1936)

⁸⁸ R. de Montigny and O. Maass, *Dominion Forest Service Bull.* 87, Canadian Dept. of Interior, Ottawa (1935)

⁸⁹ G. H. Chidester, *Paper Trade J.* 104, No. 6: 67-70 (Feb. 11, 1937)

The effect of combined on the properties of the pulp are shown in Figure IV-7, taken from work by Maass and De Montigny⁹⁰ on the cooking of black spruce at constant free sulfur dioxide (5.1%) and at constant liquor ratio (10:1). Under these conditions, the minimum critical concentration of combined was found to be 0.5%, but the liquor ratio used was about twice that normally used in commercial practice. For liquor ratios normally used, the amount of combined sulfur dioxide required in the cooking acid to prevent "burning" is at least 1.0% at the start of the cook. Stated differently, there should be between 3.5 to 5.5% combined sulfur dioxide on the basis of the wood, depending upon the species. The maximum

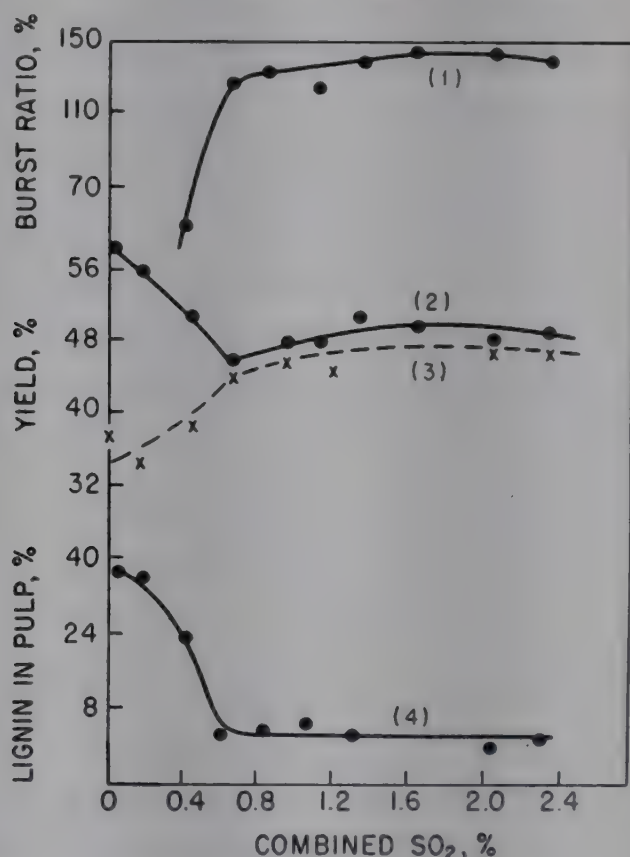


Fig. IV-7. Effect of combined sulfur dioxide on the properties of pulp:
(1) burst; (2) pulp yield; (3) cellulose yield; (4) lignin in pulp.

upper limit of combined in the cooking liquor is about 1.5% set by the limited solubility of calcium bisulfite. Combined in excess of the minimum requirement is a waste of chemical and has a deleterious effect.

It should be pointed out that here are two types of "burned" cooks, both caused from lack of combined.⁹⁰ The first type of "burning" takes place at the beginning of the cook and is caused by faulty penetration of combined. The chips are light colored and well cooked on the outside, but have dark, hard centers. The second type of "burning" takes place toward

⁹⁰ R. de Montigny and O. Maass, *Dominion Forest Service Bull. 87*, Canadian Dept. of Interior, Ottawa (1935)

the end of the cook and results from exhaustion of the available lime in the liquor. The chips are uniform in appearance and may be quite soft and readily defiberable, but they have a dark color.

Local dilution of the cooking liquor in the digester or poor local circulation of the liquor may cause a decrease in the combined in certain zones of the digester, thus leading to a loss in yield and strength of the pulp. Excessive relief can cause loss of combined by reducing the free sulfur dioxide, thus favoring the formation of the relatively insoluble calcium monosulfite. Too high a digester temperature causes loss of combined by converting calcium bisulfite into calcium monosulfite. Miller⁹¹ states that once the lignin content of the chips has been reduced below about 3%, there is no danger of burning the cook.

Use of Sodium-, Magnesium-, and Ammonia-Base Sulfite Liquors

The early investigators of the sulfite process, recognizing the technical advantages of bases other than calcium, did considerable studying of different bases.⁹² Calcium is, however, the cheapest and most abundant base and consequently has been the only base used for many years.

The use of more soluble bases in place of calcium began to attract considerable attention again in the early 1920's. It was known at the time that certain advantages are derived by the substitution of sodium, magnesium, or ammonium hydroxide for the calcium hydroxide normally used. The principal advantages are greatly reduced cooking time, easier recovery of cooking chemicals and heat, reduced stream pollution, production of more marketable by-products, and utilization of normally undesirable species. Other advantages are less danger of "burning" the cook, less danger of precipitating base during cooking, fewer screenings, and higher brightness in the unbleached pulps. So far, however, the advantages in yield, cooking time, bleachability, and strength which can be obtained with the soluble bases have not been great enough to justify the higher cost of the soluble bases, which cost about four to five times as much per ton of pulp as calcium base.⁹³ Possibilities in liquor recovery are increasing the interest in the use of soluble bases, and a few mills already have installations in operation. Sodium-base cooking liquor has been used in Sweden; the ammonia-base process is being used in Norway and the United States; the magnesium-base process is being used in the United States. Some method of liquor recovery is practiced in the sodium- and magnesium-base processes to compensate for the high chemical cost.

⁹¹ R. N. Miller, *Chemistry of the Sulfite Process*, pp. 101-112. Lockwood Trade J. Co., New York, N. Y. (1928)

⁹² J. D. Rue, *Paper Trade J.* 81, No. 16: 54-56 (Oct. 15, 1925)

⁹³ R. S. Hatch, *Pulp Paper Mag. Canada* 47, No. 9: 80-84 (1946)

Sodium base is more soluble than calcium base and hence permits a higher percentage of combined in sulfite cooking acid. It is even possible to prepare a sodium-base liquor containing free base where all the sulfur dioxide is present as monosulfite, the liquor being known as a neutral sodium sulfite liquor. Monosulfite is used in semichemical pulping, but is not used in full chemical pulping because it produces pulp of low yields and, in some cases, low strength.

When used as the base in the sulfite process, sodium produces pulp in yield and strength not appreciably different from that obtained with calcium-base liquor. Schur and Baker⁹⁴ obtained a given degree of cooking in a shorter time with sodium-base liquor than with calcium-base liquor, and the yield was slightly higher, using a mixture of spruce and balsam fir. On the other hand, Yorston⁹⁵ obtained markedly lower yields with sodium-base liquor in the region of 1 to 2% combined, but these results were obtained on sawdust cooked at a liquor ratio of 50 to 1. The low yield in this case was attributed to attack on the carbohydrates due to the low concentration of combined used. Chidester⁹⁶ found that the strengths and yields of pulps obtained with sodium-base acid pass through a maximum at 2 to 3% combined when the initial total sulfur dioxide is held constant at 6%. Reducing the combined down to 0.8% or below has less deleterious effect on pulp yield and pulp strength in the case of sodium-base liquor than in the case of calcium-base liquor.⁹⁷

A definite advantage of sodium-base liquor is the lower bleach requirement of the pulp, compared with that of regular sulfite pulp made with calcium-base acid. In certain ranges of pulp bleaching, reduction in bleach consumption of 40 to 50% can be realized by changing from calcium- to sodium-base liquor, and although such a large saving in bleach consumption is not typical, substantial savings can be made. At a given permanganate number, pulps prepared with sodium-base acid develop a higher bursting strength and a lower tearing strength than pulps produced by calcium-base liquor.⁹⁸ The pulps have slightly higher pentosan content, higher cuprammonium viscosity,⁹⁸ and slightly lower ether extract⁹⁹ than conventional pulps. Yorston¹⁰⁰ found that sodium-base liquor is much more effective

⁹⁴ M. O. Schur and R. E. Baker, *Paper Trade J.* 112, No. 20: 38-45; 115, No. 12: 129-136 (May 15, 1941, Sept. 17, 1942)

⁹⁵ F. H. Yorston, *Dominion Forest Service Bull.* 97, Canadian Dept. of Mines and Resources, Ottawa (1942)

⁹⁶ G. H. Chidester, *Paper Trade J.* 104, No. 6: 67-70 (Feb. 11, 1937)

⁹⁷ M. O. Schur and R. E. Baker, *Paper Trade J.* 115, No. 12: 129-136 (Sept. 17, 1942)

⁹⁸ M. O. Schur and R. E. Baker, *Paper Trade J.* 115, No. 12: 129-136 (Sept. 17, 1942)

⁹⁹ R. S. Hatch, *Pulp Paper Mag. Canada* 47, No. 9: 80-84 (1946)

¹⁰⁰ F. H. Yorston, "Studies in Sulfite Pulping," *Dominion Forest Service Bull.* 97, Canadian Dept. of Mines and Resources, Ottawa (1942)

than calcium-base liquor in the pulping of slow-growth pine, the screenings being reduced from 7.3 to 0.5% and the tearing strength of the pulp being appreciably higher. These effects are attributed to better penetration of the heartwood.¹⁰¹ The higher diffusion velocity of sodium ion compared with that of calcium is of value in the sulfite pulping of hardwoods.

Ammonia-base sulfite liquor was suggested for pulping in early American patents,¹⁰²⁻¹⁰⁴ and recently there has been a revived interest. Ammonia-base liquor has certain advantages over calcium-base liquor derived from the higher solubility of ammonium salts and the higher mobility of ammonium ion. The results obtained are similar to those obtained with sodium-base liquor. Ammonia-base liquor will pulp certain hardwoods not capable of being pulped by calcium-base liquor, e.g., black cherry. The advantages of ammonia-base liquor include such advantages as more rapid cooking and reduced screenings. In one commercial installation, ammonia-base sulfite acid replaced dolomite base acid for the cooking of western woods.^{104a} With the combined sulfur dioxide reduced from 1.30 to 0.85%, there was no harm to pulp quality except for color, and the mill was able to reduce digester temperature by 10° F. with an increase of 15% in pulp production and the screenings were reduced by more than one half.

Magnesium has received considerable attention as a base for sulfite cooking liquor. The first commercial sulfite mill in Sweden used magnesium as the base, and magnesium has been suggested as a base for sulfite pulping in early patents. Until lately there has been no significant use of magnesium except in a few mills employing dolomite lime, where the base is a mixture of two parts calcium and one part magnesium carbonates. Most sulfite mills use a high calcium limestone as the raw material for their base, since this works best in the tower method. In general, there is no great difference in the cooking action of calcium- and magnesium-base liquors. The logarithm of the residual lignin content of the pulp versus the time of cooking is the same for both calcium-base and magnesium-base liquors.¹⁰⁵

Magnesium-base liquor is made by reacting sulfur dioxide with slaked magnesium oxide obtained by heating magnesite (MgCO_3). Magnesium bisulfite is much more soluble than calcium bisulfite at the same partial pressure of sulfur dioxide, and hence higher combined can be obtained in mag-

¹⁰¹ R. H. McKee and D. E. Cable, *Paper Trade J.* 80, No. 17: 151-156 (Apr. 23, 1925)

¹⁰² C. F. Sammet and J. L. Merrill, U. S. 1,016,178 (Jan. 30, 1912)

¹⁰³ T. Marusawa, U. S. 1,244,525 (Oct. 30, 1917)

¹⁰⁴ C. F. Cross, U. S. 1,547,907 (July 28, 1925)

^{104a} L. A. La Fond and W. F. Holzer, talk given at 36th Annual Meeting of TAPPI, New York City, February 19-22, 1951

¹⁰⁵ F. H. Yorston, *Dominion Forest Service Bull.* 97, Canadian Dept. of Mines and Resources, Ottawa (1942)

nesium-base acid.¹⁰⁶ By carrying higher combined, it is possible to increase the yield, but the rate of delignification of spruce in magnesium-base sulfite liquor decreases markedly with increasing combined over 2 to 2.5%.¹⁰⁵ As a rule, pulps produced by magnesium-base liquors are softer and more pliable than pulps produced by calcium base. The principal advantage of magnesium-base acid is the greater ease of waste liquor recovery. The recovery of soluble-base waste liquors is discussed in a later section.

Effect of Liquor Ratio in Sulfite Process

A typical sulfite cook would be carried out at a liquor ratio of about 4.5 lb. of liquor per pound of dry wood.¹⁰⁷ This amount of liquor, together with about another pound of liquid from the moisture in the chips, represents a total of 5.5 parts of water per part of oven-dry wood. Sufficient cooking acid must be present at the start of the cook to cover the wood chips completely so that there will be no "burning." In the case of direct heated digesters some of the liquor is removed by side relief during the cook and returned to the acid storage tank.

At very low liquor ratios, there is a possibility that too little chemical will be present in the digester unless the original concentration of the liquor is very high. This is particularly important in the case of the combined sulfur dioxide, so that when low liquor ratios are used, the ratio of combined to wood may be a more important factor than the initial concentration of combined in the liquor. Any loss in combined resulting from side relief must be taken into account in calculating the amount of combined present during the cook.

The results in Figure IV-8 show the effect of liquor ratio on yield, permanganate number, and bursting strength of pulp obtained from black spruce cooked at a maximum temperature of 140° C. in a 10-hour cook with no top relief.¹⁰⁸ The cooking liquor composition was 6.0% total, 4.8% free, and 1.2% combined sulfur dioxide. These results show what happens when there is insufficient liquor to cover the chips. Under these circumstances, gaseous sulfur dioxide acts on unsubmerged chips so that sulfonation occurs in the absence of base, thereby resulting in a low yield of dark, degraded pulp of low strength and high permanganate number. Even when there was enough liquor to cover the wood, the same effects were produced to some extent because there was insufficient combined on the wood basis.

In the case of magnesium base or other soluble base, liquor ratios as low as 2.5 lb. of total liquor per pound of oven-dry wood are possible be-

¹⁰⁶ F. H. Conrad and D. B. Brice, *Tappi* 32, No. 5: 222-226 (May, 1949)

• ¹⁰⁷ E. Ott, ed., *Cellulose and Cellulose Derivatives*. Interscience Publishers, Inc., New York, N. Y. (1943)

¹⁰⁸ E. Ott, ed., *Cellulose and Cellulose Derivatives*, p. 499

cause of the higher concentrations which can be obtained.¹⁰⁹ This makes it possible to carry the liquor level in the digester low enough to avoid any side relief, which enables the operator to calculate the exact amount of combined without taking into account the loss in side relief.¹¹⁰ Such low liquor ratios make it absolutely necessary to employ forced circulation of the liquor in order to keep the chips well wetted with acid at all times. The most practical liquor ratio to use in commercial operation is generally in the range of 4 to 1, or 5 to 1, which is obtained by adding a portion of waste

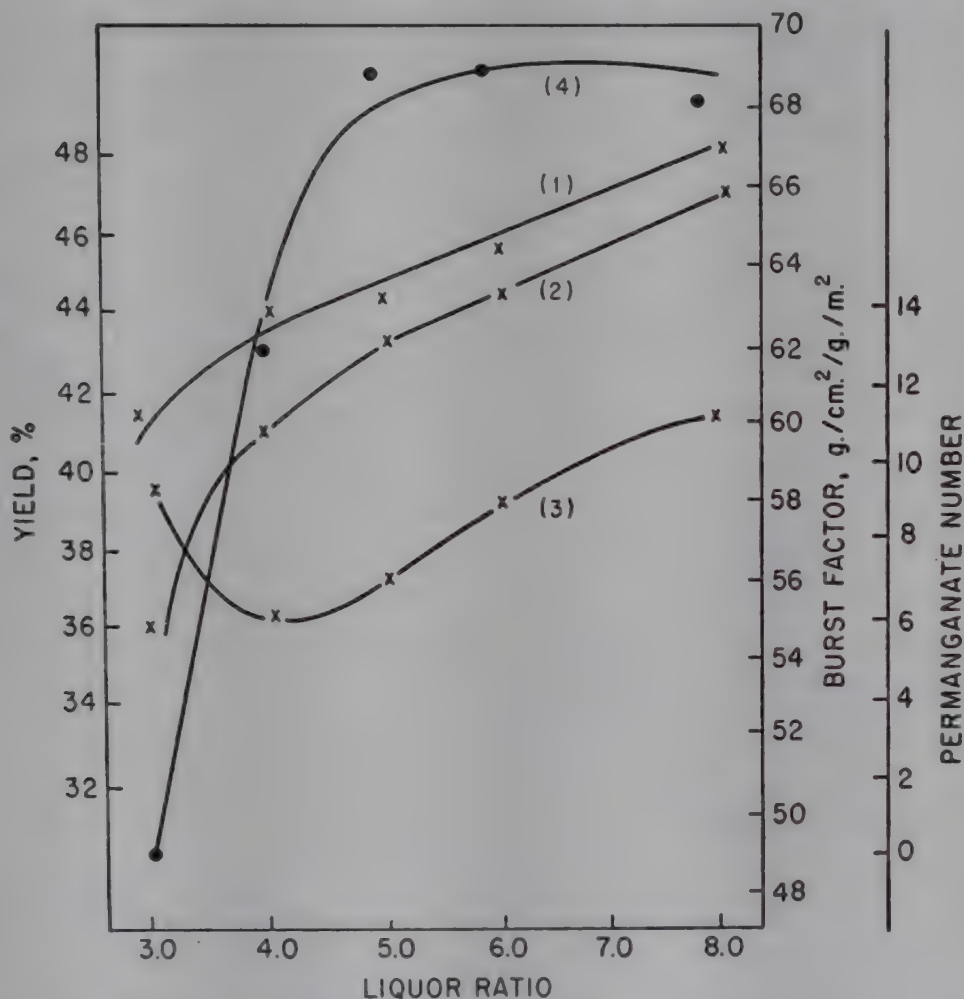


Fig. IV-8. Effect of liquor ratio in sulfite process on total yield (1), screened yield (2), permanganate number (3), and bursting strength of pulp (4). Liquor ratio = cubic centimeters of liquor per gram oven-dry wood.

liquor to the fresh acid. Lower liquor ratios have the advantage of producing stronger waste (black) liquors, thus reducing the load on the waste liquor evaporation system.

Effect of Time of Cooking in Sulfite Process

A Mitscherlich cook generally takes from 16 to 24 hours. The original Ritter-Kellner process took 15 hours, and a more recent modification,

¹⁰⁹ R. J. Hatch, *Pulp Paper Mag. Canada* 48, No. 13: 85-86 (Dec., 1947)

¹¹⁰ G. V. Palmrose, U. S. 2,192,239

known as the "quick cook," takes about 6 to 8 hours. The optimum time of cooking depends upon the composition of cooking acid, type of wood, type of pulp desired and, most important of all, the maximum cooking temperature. Commercial unbleached sulfite pulp for news is generally cooked on a 6-hour schedule, easy belaching pulp on a 9-hour schedule, and high grade pulp for dissolving purposes on a 12 to 14 hour schedule.

If the period of cooking at maximum temperature is too long, the yield of pulp is decreased, and this occurs without a corresponding improvement in the bleachability of the pulp. Under no circumstances can the cook be continued beyond exhaustion of the bisulfite. The effect of time of cooking at maximum temperature on black spruce is shown in Table V.¹¹¹

TABLE V

EFFECT OF COOKING TIME AT MAXIMUM TEMPERATURE IN SULFITE PROCESS

Time at max. temp., hrs.	Total yield, %	Screened yield, %	Perman- ganate number	Beating time, min.	Burst factor, g./cm. ² /g./m. ²
2.0	56.0	46.3	22.5	40	75
2.5	52.6	49.0	18.1	42	73
3.0	50.6	47.8	13.9	43	79
3.5	48.2	47.1	12.9	49	73
4.0	47.4	46.1	14.6	46	72

Liquor ratio, 5 cc. per gram of oven-dry wood.

Maximum temperature, 134° C.

Time to maximum temperature, 7.0 hours.

Cooking liquor composition: 6.2% total, 5.0% free, 1.2% combined.

Cooking Reactions in Sulfite Process

The reactions which occur in sulfite pulping affect the lignin, cellulose, and hemicelluloses in the wood. There are also miscellaneous reactions between the cooking chemical and minor components of the wood. The various reactions are discussed below.

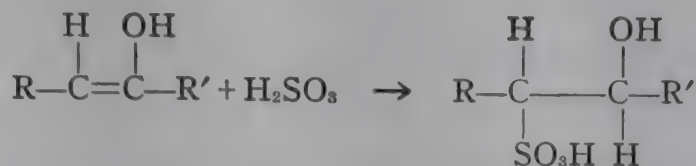
Reactions between Sulfite Liquor and Lignin

The principal reaction in the sulfite process has long been regarded as a sulfonation of the lignin. It is known that lignin combines with sulfur dioxide, but one of the important questions is the place at which sulfonation occurs in the lignin molecule. It is possible for sulfonation to take place in either the benzene nucleus or in the side chain of the lignin building unit.

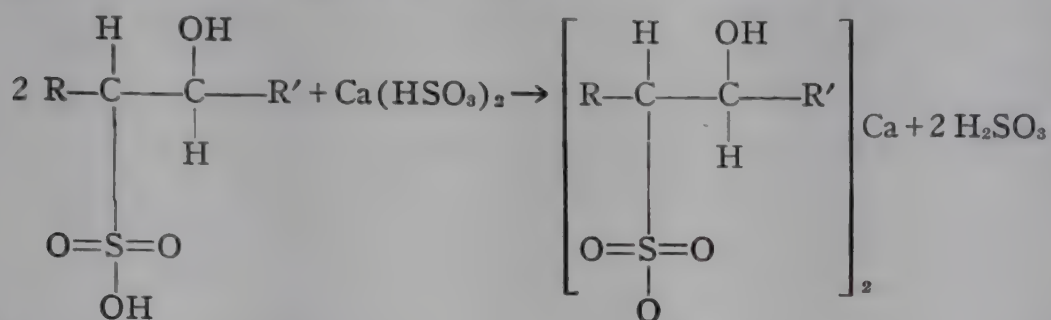
Klason advanced the hypothesis in 1893 that sulfurous acid reacts in

¹¹¹ E. Ott, ed., *Cellulose and Cellulose Derivatives*, p. 501. Interscience Publishers, Inc., New York, N. Y. (1943)

an addition reaction at an ethylenic linkage in the lignin molecule, as shown below, forming liginosulfonic acid.



This acid immediately reacts with base to form calcium liginosulfonate:



This formula is in agreement with experimental evidence previously mentioned which shows that the constituents of sulfite liquor react with wood in the proportion represented by the addition of bisulfite to an ethylene linkage. However, since the presence of ethylenic (double) bonds in lignin has not been positively established, other theories have been proposed to explain the reaction between sulfite cooking acid and lignin.

Freudenberg¹¹² postulated a two-step process, in the first step of which an oxygen linkage between two carbon atoms in the lignin molecule is ruptured to produce a phenolic hydroxyl, and in the second step of which a sulfonic acid group goes into the side chain. One of the biggest arguments against this theory of Freudenberg's is that methylated lignin can be sulfonated, but not dissolved,¹¹³ thereby indicating that an opening of the pyrane or furane ring is questionable, because it is unlikely that the methylation of two hydroxyl groups in a lignin building unit of 840 would prevent opening of the ring. Most chemists now believe that Freudenberg's theory of sulfonation involving the opening of a pyrane or furane ring is untenable. As further evidence that no new hydroxyl groups are formed, it can be shown that the sum of hydroxyl and sulfonic acid groups appears to remain fairly constant for all degrees of sulfonation. It has been shown by Hägglund and Holmberg that the methoxyl content is the same for methylated lignin from liginosulfonic acid as for methylated native lignin, which indicates that no new hydroxyl groups are formed on sulfonation. Recent work in Sweden by Lange, Erdtman, and others has shown that the ultraviolet absorption of lignin is not affected by sulfonation, thereby indicating that sulfonation

¹¹² K. Freudenberg, F. Sohns and A. Janson, *Ann.* 518, No. 1: 62-85 (May 24, 1935)

¹¹³ H. Erdtman, G. Aulin-Erdtman and B. Lindgren, *Svensk Papperstidn.* 49: No. 9: 199-200 (May 15, 1946)

does not involve a reaction with an unsaturated system. It is now fairly generally believed that the sulfonation reaction takes place with alcoholic hydroxyl groups in the lignin molecule or at a carbonyl group.¹¹⁴

Klason believed that four molecules of sulfur dioxide combine with one molecule of lignin, two strongly combined in the form of sulfonic acid and two held in some weaker association. The sulfonated lignin in commercial, well-cooked sulfite pulp contains up to 11% sulfur, equivalent to about 15% of the weight of the unaltered lignin.¹¹⁵ It is known, however, that lignin can be dissolved in suitable buffers at much lower sulfur content than this. According to Brauns,¹¹⁶ the lowest sulfur content required to render lignin soluble is in the neighborhood of 3.5%, which is approximately one sulfonic group for each building unit of 840. Erdtman¹¹⁷ points out that lignin passes into solution in sulfite cooking acid as soon as the sulfur content of the lignin is increased to about one sulfur atom per two methoxyl groups. Thus, technical lignosulfonic acids from waste liquor generally contain one sulfonic acid group for two lignin building stones, i.e., per two methoxyl groups.¹¹⁸ It is possible to obtain a degree of substitution of one sulfonic acid group per single building stone by careful isolation and further sulfonation of the lignosulfonic acid, but this high degree of sulfonation is not obtained in commercial sulfite cooking, due presumably to inactivation of hydroxyl groups in the lignin molecule.¹¹⁸ Under special conditions, sulfonated lignins have been prepared ranging from 1S to 4OCH₃ to about 1S to 1OCH₃. Different cooking conditions affect the amount of sulfonation and result in different sulfonated lignins. Erdtman¹¹⁹ has shown ultraviolet absorption curves for three lignosulfonic acids, one obtained from rayon pulp, another from regular papermaking pulp, and the third from a lightly sulfonated lignin (Kullgren acid¹²⁰). Different shaped curves were obtained for the three lignins, indicating that there is a difference in the molecular structure. Lignosulfonic acids in sulfite waste liquor can be separated into fractions of different sulfur contents. In general, the lower the sulfur content, the lower the solubility of the lignosulfonic acid. It is generally believed that the lignin dissolved in the first stage of pulping is more heavily sulfonated than the lignin dissolved later.

¹¹⁴ G. Aulin-Erdtman, A. Björkman, H. Erdtman and S. E. Hägglund, *Svensk Papperstidn.* 50, No. 11B: 81 (June 15, 1947)

¹¹⁵ C. R. Mitchell and F. H. Yorston, *Pulp Paper Mag. Canada* 37: 195-198, 209 (Mar., 1936)

¹¹⁶ F. E. Brauns, *Paper Trade J.* 111, No. 14: 33 (Oct. 3, 1940)

¹¹⁷ H. Erdtman, *Tappi* 32, No. 8: 346-348 (Aug., 1949)

¹¹⁸ H. Erdtman, *Tappi* 32, No. 2: 75-77 (Feb., 1949)

¹¹⁹ G. Aulin-Erdtman, *Tappi* 32, No. 4: 160-166 (Apr., 1949)

¹²⁰ Kullgren's lignosulfonic acids are prepared by mild conditions, using a cooking acid of pH 5, the solid wood treated with 0.01 N HCl and the free lignosulfonic acid dissolved in hot water and finally treated with sulfite cooking acid until 1S per 2.1 methoxyls is obtained.

Opinion differs somewhat as to the controlling factor in the rate of lignin dissolution in sulfite cooking. Hägglund and Johnson¹²¹ regard the sulfite process as taking place in two stages. They believe the first stage, which occurs at 60 to 70° C. when the acidity of the cooking liquor is still rather low, is a sulfonation stage in which "solid" lignosulfonic acid is produced. The second stage then involves a slow hydrolysis of the "solid" lignosulfonic acid which helps to cleave the bond between the lignin and carbohydrates and a further sulfonation of the lignin forming lignosulfonic acids which are soluble in the cooking liquor. According to Hägglund's theory, the rate of delignification is dependent upon the hydrogen ion concentration after sulfonation is complete, since this controls the rate of hy-

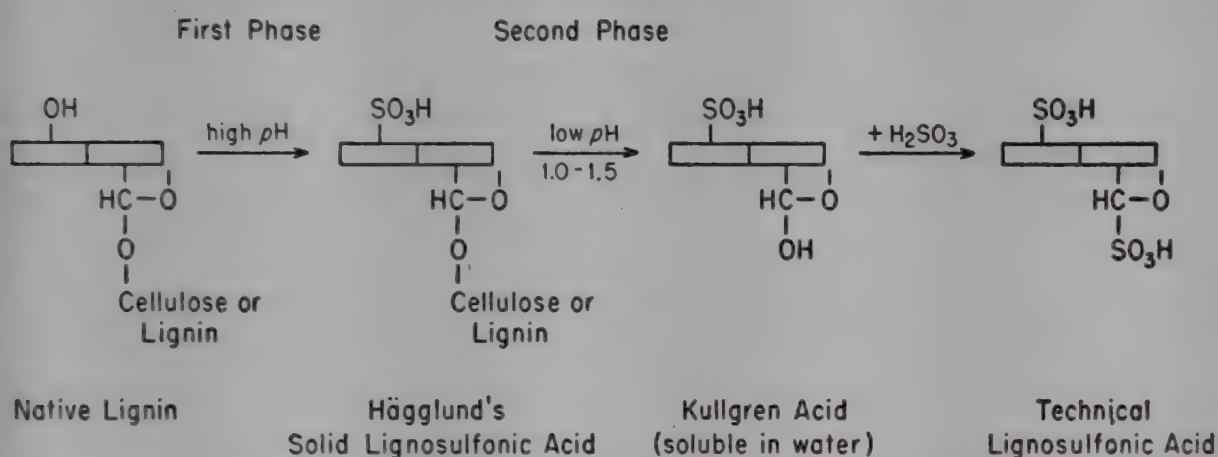


Fig. IV-9. Schematic diagram of reactions occurring in sulfite pulping.

drolysis of the lignosulfonic acid. The rate of hydrolysis is controlled by the amount of sulfur in the lignin molecule, since the molecules with the highest sulfur content are most easily hydrolyzed.¹²² As evidence of the hydrolytic nature of the reaction, it has been shown that the lignin in wood cooked with a liquor of low "free" sulfurous acid is readily sulfonated, but remains for the most part insoluble; if the pH is reduced to 1.85, over 90% of the lignin passes into solution.¹²⁴ After the lignosulfonic acid passes into solution, it is further sulfonated (according to Hägglund's theory) by the bisulfite. This secondary sulfonation depends on the concentration of bisulfite ion in the liquor. These reactions are shown schematically in Figure IV-9 where each block represents a lignin unit.^{118, 125}

¹²¹ E. Hägglund and T. Johnson, *Finnish Paper and Timber J.*: 282-288 (1934)

¹²² F. H. Yorston, Forest Prod. Lab., *Can. Pulp and Paper Lab. Quarterly Rev.* 20: 15-21 (1934)

¹²⁴ J. M. Pepper, *Pulp Paper Mag. Canada* 46, No. 2: 83-91 (Feb., 1945)

¹²⁵ Kullgren's lignosulfonic acids are prepared by mild conditions, using a cooking acid of pH 5, the solid wood treated with 0.01 N HCl and the free lignosulfonic acid dissolved in hot water and finally treated with sulfite cooking acid until 1S per 2.1 methoxyls is obtained.

Work by Maass¹²⁶⁻¹²⁹ and coworkers on the kinetics of sulfite cooking has indicated that the rate of delignification is dependent upon the partial pressure of sulfur dioxide in the cooking liquor, since a plot of the logarithm of the partial pressure of sulfur dioxide against the rate of reaction is a straight line, regardless of the amount of base in the liquor. This is shown in Figure IV-10.¹²⁶ Since the partial pressure of sulfur dioxide depends on the product of the concentration of hydrogen ions and bisulfite ions, it follows that the rate of delignification must also be dependent upon the concentration of the hydrogen and bisulfite ions or the concentration of sulfurous acid. Yorston¹³⁰ points out that the rate of delignification is proportional to the (1) concentration of sulfur dioxide in solution (SO_2), (2) concentration of sulfurous acid in solution (H_2SO_3), and (3) the product

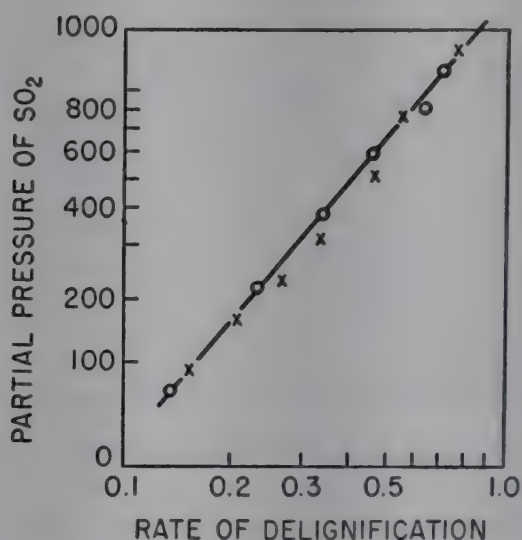


Fig. IV-10. Rate of delignification of spruce in sulfite pulping as a function of the partial pressure of sulfur dioxide. (○) 0.4% combined; (×) 0.9% combined.

of the hydrogen ion and bisulfite ion concentrations (H^+) (HSO_3^-). According to this, sulfurous acid (as ions or as molecules) is the active cooking agent in the sulfite process. The conclusions of Maass and Yorston and coworkers thus disagree with Hägglund's, inasmuch as they believe that sulfonation takes place in a gradual process (and not rapidly, as Hägglund

¹²⁶ J. M. Calhoun, F. H. Yorston and O. Maass, *Can. J. Research* 15B: 457 (1937)

¹²⁷ J. M. Calhoun, J. J. R. Cannon, F. H. Yorston and O. Maass, *Can. J. Research* 16B: 242 (1938)

¹²⁸ J. M. Calhoun, F. H. Yorston and O. Maass, *Can. J. Research* 17B: 111 (1939)

¹²⁹ C. K. White, J. E. Vivian and R. P. Whitney, *Paper Trade J.* 126, No. 20: 242-244 (May 13, 1948)

¹³⁰ F. H. Yorston, *Dominion Forest Service Bull.* 97, Canadian Dept. of Mines and Resources, Ottawa (1942)

believed) and that the rate of reaction is controlled by the rate of sulfonation (and not by the rate of hydrolysis, as Hägglund believed).

Since the active cooking chemical is present in excess, the rate of reaction in sulfite cooking should be proportional to the amount of unreacted lignin in the wood, the accessibility of the lignin to the cooking acid, and the rate of diffusion of soluble products out of the wood. This mechanism suggests a first order reaction in which the rate of lignin removal is approximately equal to a constant times the amount of unreacted lignin. However, the reactions involved are heterogeneous in nature and therefore cannot be expected to follow a reaction of definite order. According to the results of Goldfinger,¹³¹ the order of reaction in sulfite cooking varies from a high value at the beginning of the cooking cycle, decreases to nearly zero at an intermediate stage, and then increases again to a high value toward the end. The energy of activation of the lignin removal is low at the beginning, but starts to increase at a delignification of about 40%. Yorston¹³⁰ has shown under special conditions that the logarithm of the amount of lignin remaining in the pulp (calculated as per cent of the wood weight) bears a straight-line relationship with the time of cooking, except in the early stages of the cook.

The temperature of cooking has an important effect on the rate of lignin removal. In the Ritter-Kellner process, the lignin is removed rapidly as soon as the temperature is raised over 110° C., and continues to be removed at a decreasingly lower rate until the end of the cook. In the Mitscherlich process, the lignin is not removed at a rapid rate until the cook has been in progress for 7 to 9 hours, because very often the temperature does not exceed 110° C. in the Mitscherlich process until this time. Kullgren has shown that the insoluble lignosulfonic acids (washed free of calcium) in strong sulfite pulp will pass slowly into solution when heated to about 80 to 100° C.

In the sulfite process, the lignin seems to be removed for all practical purposes simultaneously from the middle lamella and the secondary walls of the fiber.^{132, 133} Recent work by Lange in which he took photomicrographs of thin cross sections of chips at various stages of cooking showed the middle lamella lignin to be attacked rapidly in early stages of the cook.

Effect of Sulfite Cooking on Hemicelluloses

Until recent times, hemicelluloses were regarded as an undesirable part of the cellulose fiber; the most desirable fiber for papermaking pur-

¹³¹ G. Goldfinger, *Paper Trade J.* 112, No. 24: 289-291 (June 12, 1941)

¹³² A. L. M. Bixler, *Paper Trade J.* 107, No. 15: 171-182 (Oct. 13, 1938)

¹³³ A. L. M. Bixler, *Paper Trade J.* 105, No. 27: 37-38 (Dec. 30, 1937)

poses was believed to be one containing 100% pure cellulose. This theory is fallacious, since it is now known that hemicelluloses play a definite role in papermaking and, in fact, a satisfactory paper cannot be formed from wood pulp without some hemicellulosic material being present. The best pulp is one which has been cooked to remove most of the lignin, but not so drastically cooked as to degrade the cellulose or remove too much of the hemicellulose fraction. Such a pulp will beat easily and have good strength characteristics, because a high proportion of the rapid-beating hemicelluloses are left in the pulp. Because of the relationship between the hemicellulosic content and the papermaking qualities of the pulp and also because of the economic factors involved, pulp chemists have turned their attention to the production of pulps containing the highest possible proportion of the carbohydrate constituents of the original wood.

Carbohydrates can be removed from wood without much lignin removal, but it is considered impossible to remove lignin without considerable carbohydrate removal. Both classes of hemicellulose, i.e., the polyuronides and the celulosans, are attacked in the sulfite process, but the polyuronides are attacked to the greatest extent. A large part of the total polyuronides are removed, since they are associated with the lignin (the presence of carbon dioxide in the relief gases being due mostly to the decomposition of the polyuronide fraction of the hemicelluloses). A substantial part of the celulosans remains with the fiber, although if conditions are drastic enough, they may also be removed to a large extent.

Sulfite cooking liquor attacks the carbohydrates in wood in the same manner as dilute mineral acids.¹³⁴ This is shown by the fact that the copper number and hot alkali solubility of the pulp increase simultaneously with decreasing viscosity of the pulp, as would be expected when acid hydrolysis occurs.¹³⁵ As a result of this acid hydrolysis of the hemicelluloses, sugars are always present in sulfite waste liquor. Commercial waste liquor from spruce contains from 3.2 to 3.8% sugar, which amounts to about 10 to 15% of the weight of the wood. Some of the sugars (mannose and glucose) are fermentable and can be converted into alcohol; the principal unfermentable sugar produced is xylose. Some of the sugars produced by hydrolysis form addition compounds with sulfite which are non-fermentable.¹³⁶

During the early stages of a sulfite cook, hemicelluloses are removed at a greater rate than the lignin, but this lessens as the less resistant hemicelluloses are removed. Degradation of hemicelluloses is particularly no-

¹³⁴ R. N. Miller, W. H. Swanson and R. Soderquist, *Chemistry of the Sulfite Process*, pp. 80-91. Lockwood Trade J. Co., New York, N. Y. (1928)

¹³⁵ O. Samuelson, I. Bernson and S. O. Regestad, *Svensk Kem. Tid.* 61, 234 (1949) through O. Samuelson and C. Ramsel, *Svensk Papperstidn.* 53, No. 6: 155-162 (Mar. 31, 1950)

¹³⁶ E. Adler, *Svensk Papperstidn.* 49, No. 15: 339-346 (Aug. 15, 1946)

ticeable if the cooking time is too long, the concentrations of chemical too great, or the temperature too high, high temperatures being particularly degrading. Hydrolysis of carbohydrates to sugars is fairly rapid at temperatures over 100° C. Runkel¹³⁷ has pointed out the desirability of shortening the time of cooking in order to prevent excessive hydrolysis of the hemicelluloses.

When the temperature and time of cooking are held constant, the acidity of the liquor appears to be the most important factor affecting the loss of carbohydrate.¹³⁸ Sugars are formed more rapidly in the Ritter-Kellner process and in greater yield than in the Mitscherlich process because of the higher percentage of free sulfur dioxide (and the higher temperatures which are used). The base in the cooking liquor has a moderating effect on the hydrolysis of carbohydrates. Hägglund obtained 21% sugar when he cooked wood with a liquor containing no base.

The sulfite process has more degrading effect on the hemicelluloses than the alkaline cooking processes (soda and sulfate). The hemicellulosic materials left in sulfite pulp are more easily hydrated, and consequently sulfite pulps tend to form sheets of higher transparency than either soda or sulfate pulps. The degraded celluloses and hemicelluloses left in sulfite pulp are not soluble in the acid cooking liquor, but are soluble in weakly alkaline solutions.¹³⁹ Consequently, sulfite pulps which are extracted (purified) with alkali have an exceedingly low pentosan content and high alpha cellulose content, the pulps being suitable for making cellulose derivatives. Such extracted pulps form papers of outstanding softness and flexibility, on account of their low pentosan content.

Effect of Sulfite Cooking on Cellulose

The properties of cellulose are determined by the chain length of the cellulose molecules. Even with the mildest cooking conditions, sulfite cooking liquor exerts a degrading influence on the cellulose molecules so that the very short molecules are dissolved and removed during cooking, and the very long molecules are degraded into ones of medium chain length. In one sense, this homogenizing action is desirable, since it tends to reduce the average chain length of the cellulose molecules and thereby tends to increase the ease of beating of the pulp. Heuser¹⁴⁰ reports that the average D.P. of spruce cellulose is reduced from an original value of about 2400 to about 2000 when pulped by the Mitscherlich process, and to about 1400 when the quick cook is used.

¹³⁷ R. Runkel, *Zellstoff u. Papier* 10, No. 9: 773-775 (Nov., 1930)

¹³⁸ F. H. Yorston, *Dominion Forest Service Bull.* 97, Canadian Dept. of Mines and Resources, Ottawa (1942)

¹³⁹ G. A. Richter, *Paper Trade J.* 101, No. 19: 276-280 (Nov. 7, 1935)

¹⁴⁰ E. Heuser, *Tappi* 33, No. 3: 118-124 (Mar., 1950)

In the early stages of a sulfite cook, equal parts of cellulose and lignin appear to be removed. Bray and Andrews¹⁴¹ found that, in using a liquor containing 5.6% total SO₂ and a maximum temperature of 137° C., the lignin and cellulose contents of sulfite pulp were approximately the same as that of the original wood up to the ninth hour of cooking. During the remainder of the cooking period, the lignin is removed at a greater rate than the cellulose. Toward the end of the cook, the yield of alpha cellulose on wood weight passes through a maximum.¹⁴²

After the lignin is fairly well removed, further cooking destroys the cellulose without increasing the purity of the pulp.¹⁴³ Increasing the temperature tends to increase the rate of degradation of the cellulose at a proportionately higher rate than it does of the lignin, and thus, extremely high temperature must be avoided, since they result in very low pulp yields. Pulps of unusually high alpha cellulose content can be produced by cooking at a high temperature for a short time, but the yield is low.¹⁴⁴ The best method of reducing attack on the cellulose and still obtain a bleachable pulp is to use strong acid, low cooking temperature, and relatively short cooking time.

Mark and Goldfinger¹⁴⁵ point out that one of the reasons wood pulps are more susceptible to degradation than cotton pulps is the drastic treatment with acid and high temperature which they receive in the cooking operation. Purified wood pulp may, under certain conditions, have as high an initial viscosity as cotton pulp, but wood pulp is more susceptible to chemical attack, due to weakened linkages in the cellulose chain.

The degradation of cellulose which occurs during cooking can be readily determined by the cuprammonium viscosity test, although this test is not commonly used as a guide in pulp mill operation. Nearly all mills use a bleachability test (permanganate number or chlorine number) as a criterion of cooking to measure the amount of lignin and other readily oxidizable impurities in the pulp. Rich¹⁴⁶ reports that in order to obtain the same viscosity with white fir pulp as with hemlock, it is necessary to cook to a higher bleachability, i.e., to cook the fir less.

Miscellaneous Reactions during Sulfite Pulping

It is well known that wood heated to 135 to 140° C. in the presence of water is difficult to delignify because of the resinification of lignin mole-

¹⁴¹ M. W. Bray and T. M. Andrews, *Chemistry of the Sulfite Process*, Chapter II, pp. 23-31. Lockwood Trade J. Co., New York, N. Y. (1928)

¹⁴² E. Hägglund, *Svensk Papperstidn.* 41: 523 (1938)

¹⁴³ S. D. Wells, R. H. Grabow, J. A. Staidl and M. W. Bray, *Paper Trade J.* 76, No. 2: 49-55 (June 14, 1923)

¹⁴⁴ G. Jayme and L. Groggaard, *Papier-Fabr.* 38, No. 18: 101-108 (May, 1940)

¹⁴⁵ H. Mark and G. Goldfinger, *Paper Trade J.* 115, No. 203-205 (Oct. 15, 1942)

¹⁴⁶ E. D. Rich, *Paper Trade J.* 112, No. 6: 63-68 (Feb. 6, 1941)

cules in the wood. Wood which has been heated to high initial temperatures in the absence of free sulfurous acid (or sufites) cannot be delignified in sulfite liquor.¹⁴⁷ On the other hand, if the wood is first sulfonated before heating, the lignin can be satisfactorily removed by subsequent hydrolysis.

Recent studies have indicated that substances found in the heartwood in small quantities in certain species, e.g., pines and Douglas fir, have an inhibiting effect on pulping of the wood by the sulfite process. The sapwood of these species can be satisfactorily pulped, indicating that the offending substances are present only in the heartwood. Extracting the heartwood with ether or benzene does not improve the pulping, illustrating that impregnating resins are not the primary cause of the non-digestibility.¹⁴⁸ On the other hand, if the benzene-extracted wood is subsequently extracted with alcohol or acetone, the wood can be pulped normally. The offending substances are believed to be aromatic compounds belonging to the class of stilbenes or flavones. Phenolic compounds (e.g., dihydroxystilbene and the monomethyl ether of dihydroxystilbene) have been found in the heartwood of European pine, *Pinus sylvestris*, to the extent of about 0.8% of the weight of the wood.¹⁴⁹⁻¹⁵¹ A flavone (3,3',4',5,7-pentahydroxyflavone) has been found in the heartwood of Douglas fir, generally to the extent of about 1% of the weight of the heartwood, although up to 2.2% was found in one sample.¹⁵² These phenolic compounds undergo a rapid condensation with lignin at the high temperature and low pH of a sulfite cook to form condensed lignin products of low solubility. The condensed products can be sulfonated, but the sulfonated products are resistant to the solubilizing hydrolysis reaction.¹⁵³ As little as 0.5 to 1.0% of these compounds is sufficient to render the lignin insoluble in the cooking liquor. Erdtmann¹⁵¹ reports that spruce logs left in the mill pond for a long time with the bark on develop a shell of resistant wood, owing to the migration of phenolic substances from the bark into the outer layers of the wood. Sodium-base cooking liquors¹⁵⁴ and the use of cooking acid containing a high percentage of free sulfur dioxide¹⁵⁵ are some of the means suggested for the pulping of these resistant woods. Pine heartwood can be pulped

¹⁴⁷ G. A. Richter, *Tappi* 32, No. 12: 553-559 (Dec., 1949)

¹⁴⁸ H. Erdtman, *Tappi* 32, No. 7: 303-304 (July, 1949)

¹⁴⁹ H. Erdtman, *Ann.* 539: 116 (1939)

¹⁵⁰ H. Erdtman, *Cellulosechemie* 18: 83 (1940)

¹⁵¹ H. Erdtman, *Svensk Papperstidn.* 43: 241 (1940)

¹⁵² J. C. Pew, *Tappi* 32, No. 1: 39-41 (Jan., 1949)

¹⁵³ G. A. Richter, *Tappi* 32, No. 12: 553-559 (Dec., 1949)

¹⁵⁴ G. H. Chidester and J. N. McGovern, *Paper Trade J.* 110, No. 10: 39-42; 113 No. 16: 32-35 (Mar. 7, 1940, Aug. 28, 1941)

¹⁵⁵ E. B. Brookbank, *Paper Trade J.* 108, No. 7: 30-38 (Feb. 16, 1939)

readily if thoroughly penetrated by acid bisulfite below 110° C. and if the temperature of the cook does not exceed 135° C.

The effect of catalysts on sulfite cooking has been studied to some extent. The presence of free sulfur or selenium in the cooking acid supposedly acts as a catalyst which decomposes the calcium bisulfite. This tends to remove base from solution by forming insoluble calcium sulfate, with the result that insufficient base is present to prevent polymerization of lignin molecules. Consequently, the presence of these materials is considered undesirable. Within recent times, special aromatic oils derived from petroleum and emulsified in water have been tried for treating the wood chips before cooking by the sulfite process.¹⁵⁶ It is claimed that these materials increase the rate of cooking and reduce pitch trouble, particularly when the wood is cooked by the Mitscherlich process.

Characteristics of Sulfite Pulp

The species favored for sulfite pulping in the eastern and lake states of the United States are the black, red, and white spruces, balsam fir, and to a smaller extent, eastern hemlock. Balsam fir tends to produce a stronger pulp than spruce,¹⁵⁷ but the yield is lower per cord of wood, the pulp sometimes causes serious pitch trouble at certain times of the year, and the paper produced is more transparent than spruce. The species favored in the western regions of the United States are western hemlock, white fir, and Sitka spruce. Western spruce produces a good, clean pulp, but tends to chip with difficulty and produces a "pitchy" pulp.¹⁵⁸ Larch gives 10% less yield than the other species. It is hard to pulp and is difficult to screen because of its long fibers.

In general, the pines have been little used for sulfite pulping because of their high resin content and resistant heartwood. However, at least one mill has used the sulfite process on southern pine, and some jack pine has been cooked by the sulfite process in the lake states. Jack pine can be pulped with calcium-base liquor by cooking with a liquor containing a relatively high sulfur dioxide concentration for a long cooking time at low temperature. Most mills, however, object to jack pine because it tends to produce a pulp which contains red or brown shives. Douglas fir is not well suited to the sulfite process because the calcium base precipitates suddenly toward the end of the cook. The use of sodium-base liquor, high free sulfur dioxide, low temperature, and longer impregnation period helps to prevent

¹⁵⁶ Socony-Vacuum Oil Co., Inc., Brooklyn, New York.

¹⁵⁷ H. J. Ostrowski, *Pulp Paper Mag. Canada* 44, No. 11: 807-809 (Oct., 1943)

¹⁵⁸ L. C. Kelley, *Pulp Paper Mag. Canada* 48, No. 3: 115-122, Convention Issue (1947)

this condition,¹⁵⁹ but in general, the resulting pulp is inferior to that obtained from other species.

Softwood sulfite pulp is light colored and contains a comparatively small amount of lignin. Freshly blown pulp turns a reddish brown when exposed to air, on account of oxidation of lignin and coloring matter remaining in the pulp. The pulp has a comparatively high resin content, since the acid cooking liquor does not remove the resinous matter found in the wood. The content of polyuronides is low, but large amounts of celulosans are present.

Sulfite pulp has medium strength and good sheet-forming properties, although these properties depend somewhat upon the nature of the cook. As a general rule, the pulp "hydrates" very readily on beating, usually requiring between one to three hours for maximum strength. Normally, pa-

TABLE VI
AVERAGE ANALYSES OF COMMERCIAL UNBLEACHED AND BLEACHED
SOFTWOOD SULFITE PULPS
(Based on oven-dry weight)

	Unbleached sulfite	Bleached sulfite
Ash, %	0.4	0.3
Ether soluble, %	0.4	0.4
Lignin, %	1.9	0.5
Pentosans, %	5.1	5.4
Cross and Bevan cellulose, %	94.7	..
Alpha cellulose, %	79.3	84.4
Alkali solubility (7.14%), %	22.2	20.2
Permanganate number	13.6	1.1
Copper number	3.1	2.6
Viscosity, cuprammonium (TAPPI), cps.	84.2	24.4

pers made from sulfite pulps are characterized by high bursting strength; this property can be improved further by using slightly undercooked pulp in order to maintain a high hemicellulosic content. Mitscherlich sulfite pulps, for example, make very strong and exceedingly tough papers. Sulfite pulps do not have as high tearing strength as sulfate pulps prepared from the same wood, but a fairly high tearing resistance can be obtained by thorough cooking. Average analyses of several commercial unbleached and bleached sulfite pulps are given in Table VI.¹⁶⁰

The commercial grades of unbleached sulfite pulps are generally classified as follows:¹⁶¹ prime strong, strong bleachable, easy bleaching, glassine

¹⁵⁹ E. B. Brookbank, Jr., *Paper Trade J.* 108, No. 7: 30-38 (Feb. 16, 1939)

¹⁶⁰ S. I. Aronovsky and E. C. Dryden, *Paper Ind.* 22, No. 3: 253-256 (June, 1940)

¹⁶¹ A. C. Hill, *Pulp Paper Mag. Canada* 49, No. 6: 77-78 (May, 1948)

type. Prime strong unbleached sulfite is the strongest grade of unbleached sulfite and is used in groundwood printing papers, wrapping tissues, folding boxboards, and other grades requiring high strength. Strong bleachable sulfite is generally sold to paper mills who wish to do their own bleaching. It has a fairly low chlorine number and, after bleaching, produces very strong, white papers suitable for waxing and wrapping tissues. Easy bleaching sulfite is a very soft, clean pulp which is suited for tissues, book papers, or any use where softness is more important than strength. Glassine type sulfite is used for the manufacture of glassine or greaseproof paper where high strength and ease of hydration are paramount. This grade is best produced by the Mitscherlich process or by other variations of the normal sulfite process. The bleached grades of sulfite pulp are generally classed as strong bleached, soft bleached, and rayon grades. The strong bleached sulfites are used where both high strength and good color are required, as in bag and wrapping papers, bonds, bristols, waxing, and other similar grades. The soft bleached grades are used where softness is more important than strength, as for tissues, book, and blotting. The rayon grades or high alpha pulps are used for making rayon or other cellulose derivatives, as a filler in plastics, and in some cases, for making special grades of paper. These are highly purified pulps characterized by uniform viscosity and high alpha cellulose content.

In the past, only coniferous woods (mostly spruce) were cooked by the sulfite process. However, because of the growing scarcity of softwoods, hardwoods have come into fairly common use; both low-density and high-density hardwoods are used. In the case of low-density hardwoods (e.g., aspen), the weight of the chips charged to the digester is less than that of spruce chips, but the yield of pulp per digester is about the same because of the higher cellulose content. The time for penetration of cooking acid is about the same as that for spruce, but the cooking time is shorter because of the faster pulping rate and lower initial lignin content.¹⁶² On the other hand, high-density hardwoods (e.g., birch) absorb only about 50% as much cooking liquor as absorbed by spruce. This means that insufficient chemical will be present during cooking unless additional liquor diffuses into the chips. Hardwoods of high density can be penetrated and pulped fairly readily by the sulfite process if the wood is thoroughly seasoned and has a moisture content below 35% of the wet weight of wood, or if the cooking liquor contains a higher-than-ordinary chemical concentration. To prevent shivy pulp, it is generally necessary to bring the digester to cooking temperature more slowly than when cooking spruce so that additional calcium bisulfite can diffuse into the chips before maximum cooking tempera-

¹⁶² J. N. McGovern, E. R. Schafer and J. S. Martin, 1947 *TAPPI Monograph Series No. 4*: 130-152, Forest Products Laboratory Report R1675.

ture is reached.¹⁶³ Generally, a 4- to 5-hour penetration period is sufficient, but some European mills cooking beech use an impregnation period as long as 12 hours, which, of course, greatly extends the cooking cycle.¹⁶⁴ A two-stage cooking process for hardwoods has been suggested by Richter¹⁶⁵ in which the chips are first impregnated with sodium sulfite and then cooked in sulfurous acid liquor. In some cases, birch is cooked in combination with hemlock, since the pulping characteristics of these two species are similar.

The properties of hardwood sulfite pulp are quite different from the softwood variety and are also quite different from the same wood cooked by the soda process. Hardwood sulfite pulps have short fiber length and, in general, have bursting and tearing strengths which are between 50 to 80% of the bursting and tearing strengths of spruce sulfite pulp. Paper birch is the best of the hardwoods in this respect, often running in bursting

TABLE VII

ANALYSIS OF COMMERCIAL SWEDISH HARDWOOD SULFITE PULPS

	Birch	Aspen
Pentosans	8.2	7.5
Viscosity (TAPPI)	61	74
Brightness (G. E.)	90.5	91.5
Freeness (S R after 60 minutes)	40	34
Breaking length, m.	7300	6600
Burst, kg./cm. ²	5.4	4.4
Tear factor	76	60
Folding	500	200

strength up to 80% and in tearing strength up to 90% of spruce pulp. Aspen pulp is the weakest of the commonly used hardwoods, being about 50 to 60% as strong as spruce. An analysis of Swedish hardwood sulfite pulps of high, bleached quality is shown in Table VII.¹⁶⁶ Hardwood sulfite hydrates much more easily than the same wood cooked by the soda process and because of its greater hydrating ability, tends to form stronger, denser, more ratty paper. Hardwood sulfite pulps do not produce as opaque paper as hardwood soda pulp. Hardwood sulfite pulps are usually bleached because they are generally too dirty and contain too many shives to be used unbleached. Bleaching can be done in one or two stages. Bleached hard-

¹⁶³ F. H. Yorston, *Dominion Forest Service Bull.* 97, Canadian Dept. of Mines and Resources, Ottawa (1942)

¹⁶⁴ J. N. McGovern and G. K. Dickerman, *Pulp Paper Mag. Canada* 47, No. 5: 80-82 (May, 1946)

¹⁶⁵ G. A. Richter, *Ind. Eng. Chem.* 33, No. 1: 75-83; No. 4: 532-538; No. 12, 1518-1528 (Jan., Apr., Dec., 1941)

¹⁶⁶ Tech. Division, Mo. Domsjo AB, Sweden, through Pagel, Horton and Co., Inc.

wood pulps are sometimes used mixed with regular bleached softwood sulfite in high-grade book and magazine papers where they have the beneficial effect of improving the formation and surface texture. They make excellent glassine papers, although the strength is not so good as paper made from softwood sulfite.¹⁶⁷ One advantage of hardwood sulfite over the softwood variety is the lower resin content, although if not properly seasoned, birch and poplar are “pitchy” because of fats and waxes in the wood. Hardwood sulfite pulps can be used in viscose manufacturing if extracted with sodium hydroxide strong enough to remove the high percentage of hemi-cellulosic material.

The yield of sulfite pulp from spruce is usually between 45 to 50% of the weight of the air-dry wood. News grade is made in yield of about 47%, book and writing grades in yield of 44.5 to 46.0%, and chemical grades in yield of about 43.5%. To make a ton of average unbleached sul-

TABLE VIII
YIELDS OF VARIOUS SPECIES COOKED BY SULFITE PROCESS

Kind of wood	Yield of oven-dry screened pulp, %
Spruce	45
Balsam fir	47
Eastern hemlock	42
Western hemlock	45
Birch	45
Maple	42
Black and red gum	42

fite pulp, 1.7 to 2.3 cords of wood are required, depending upon the density. Comparison of yields of bleachable sulfite pulp obtained from different species is given in Table VIII.¹⁶⁸ Yield is greatly affected by time and temperature (see Figs. IV-4 and IV-5) of cooking, by the concentration of combined sulfur dioxide in the cooking acid (see Fig. IV-7), and by the liquor ratio (see Fig. IV-8), but it is not appreciably affected by the amount of sulfur dioxide used in cooking. McGovern^{168a} reports that optimum strength is obtained at yields of about 50% but that good strength relative to the optimum is obtained up to a yield of almost 60%.

Recovery of Chemicals in Sulfite Process

The amount of sulfur consumed in the sulfite process varies from 110 to 120 lb. per ton of pulp in the Mitscherlich process to 150 to 300 lb. per

¹⁶⁷ J. A. Feola and C. E. Libby, *Paper Trade J.* 123, No. 13: 146-154 (Sept. 26, 1946)
¹⁶⁸ *Chemipulp Sulfite Mill Operation*, pp. 104-107. Chemipulp Process, Inc., Wauertown, N. Y. (1939)
^{168a} J. N. McGovern, *Tappi* 33, No. 10: 486-489 (Oct., 1950)

ton in the Ritter-Kellner process. The excess sulfur dioxide which is present during cooking is recovered from the relief gases so that the sulfur dioxide of the spent liquor is generally less than 0.1%. The steam consumption in the sulfite process varies from about 3,600 lb. to 6,500 lb., depending upon the method of cooking and whether a hot or cold acid system is used. The lime consumption is about 150 to 200 lb. per ton of pulp.

Recovery of Sulfite Turpentine from Relief Gas

Crude cymene is present in the relief gas obtained from the sulfite pulping of spruce. The crude product, which contains about 80% pure paracymene ($C_{10}H_{14}$) is present in both the top relief gas and the side relief liquor and is usually returned to the raw acid system, where it floats on the surface as a light yellow oil. This product, which is sometimes called spruce or sulfite turpentine, occurs to the extent of 0.4 to 1.0 gal. per ton of pulp. It can be recovered by skimming off the raw acid tank. The amount obtained depends upon the species of spruce, resin content, seasonal characteristics, and amount of aging of the wood. There have been no important commercial uses for this material (unlike sulfate turpentine), and hence the production is rather insignificant. When recovered, the crude product is generally purified by alkali treatment and steam distillation.

Recovery of Sulfur Dioxide and Heat from Blowpit Gases

In the conventional method of blowing a sulfite digester, the gases from the blowpit are allowed to escape to the atmosphere. These gases contain principally steam, air, and sulfur dioxide, but there are also small amounts of methanol, ethanol, cymene, acetone, ammonia, and other gases. If the gases are allowed to escape to the atmosphere, there is a loss of about 25,000 lb. of steam and 2,000 lb. of sulfur dioxide for each 20-ton digester blown.¹⁶⁹ This not only represents an economic loss but also constitutes a nuisance to the surrounding neighborhood.

Installations of equipment have been made in certain mills to recover a large part of the heat and sulfur in the gases from the blowpit. The process consists of passing the blowpit gases through a countercurrent flow condenser to condense the steam, which is collected in a hot-water accumulator. The non-condensing gases are next cooled, and the sulfur dioxide present in these gases is absorbed in a countercurrent packed absorption tower and absorption stack. The sulfur dioxide recovered in this step is used in the acid plant as make-up in the Jenssen towers. The process is said to save 40 lb. of sulfur and 950 lb. of steam (225 lb., 40° superheat) per air-dry ton of bleached sulfite pulp.¹⁶⁹ In most mills, hot water obtained

¹⁶⁹ N. W. Coster, L. M. Johnson and R. I. Thieme, *Pulp and Paper* 23, No. 1: 34-47 (Jan., 1949)

from blowdown steam has little use around the mill, although in some cases it may be used to heat the raw acid on the way to the hot acid accumulator.

Washing of Sulfite Pulp

After the pulp is cooked, it must be washed thoroughly with water to remove any soluble residues. These residues, if left in the pulp, cause a reversion of color, foaming, pitch trouble, and other operational difficulties on the paper machine. They also increase the bleachability and decrease the strength of the paper made from the pulp. Good washing is one of the important factors in producing a pulp of low resin content and other acceptable qualities.

The contents of the digester at the end of the cook still retain very nearly the shape of the original wood chips, being held together where the primary walls are in contact. In American mills, this situation does not exist for long, inasmuch as the contents are blown from the digester at about 20 to 50 lb. pressure, with the result that the sudden release of steam and coincident agitation causes complete disintegration of the chips into a fibrous state. One exception is the Mitscherlich process which is not blown into a fibrous state. In the Scandinavian method also, the digester is not blown, but instead the liquor is relieved and passed through heat exchangers to recover as much of the heat as possible, because the high cost of fuel makes heat a more important item than in American mills. When all the liquor is removed in this way, the wood is taken out while still in chip form and disintegrated in special tanks before washing.

In American mills, the pulp is first drained into blowpits which have $2\frac{1}{2}$ to 3 times the capacity of the digester. As much of the concentrated liquor as possible is removed in the blowpit, and then the pulp is washed in diffusers or pans to remove the solubilized lignin and other impurities. Some of the older mills still wash in the blowpit, but the most complete washing is achieved by the use of vacuum type filters in two or more stages with the filters in series. Countercurrent washing is almost universal on sulfate pulps and is gaining in use in sulfite pulps. There has been a recent trend toward four-stage washing, which is proving economical. In some cases, knotters are used ahead of the washers to improve washing efficiency. In Swedish mills, the pulp may be washed in the digester using dilute waste liquor for the initial washing. Washing should follow as soon as possible after cooking, inasmuch as the stock adsorbs coloring matter which is hard to remove if the pulp is allowed to stand in contact with the spent liquor for long periods of time.

Complete washing is a difficult, if not impossible, thing to achieve commercially, because the pulp fibers form an excellent filtering mat which

tends to hold back suspended matter in the waste liquor. The fibers also tend to adsorb coloring matter.

The effectiveness of the washing operation depends on the amount and temperature of water and the depth of the stock in the wash pit or on the filter mat of the vacuum washer. Hot water provides better washing than cold, although cold water will remove impurities as well as hot water if enough time is allowed. Washing with water up to 160° F. is advocated for best results. Channeling of water through the stock should be avoided. On vacuum filters, the vacuum, formation of cake, and shower water should be as uniform as possible in order to form an even cake. Actually, the operator has very little control over the vacuum in a vacuum filter so that the essential thing is to keep a uniform tonnage rate over the machine, in which case the filter will pretty much take care of itself.

The electrolyte content and pH of the water used in the washing operation has a bearing upon the ash content of the pulp. Calcium and magnesium ions found in hard waters cause trouble by coagulating the resins on the fiber, thus making them difficult to wash from the pulp. Lang and Laurin¹⁷⁰ report that between 15 to 35 p.p.m. of sodium hexametaphosphate in the wash water will increase the efficiency of washing of chemical pulps, particularly sulfite pulp. It is generally true that the softer the water, the more efficient the washing.

The important chemical tests on sulfite waste liquor are specific gravity, total solids, sulfated ash, lime, magnesia, total sulfur, free sulfur dioxide, loosely combined sulfur dioxide, sulfur trioxide, volatile acids, alcohols and acetone, lignin, furfural, pentoses, and total sugars. The methods of making these determinations are described in TAPPI Standards and other sources.¹⁷¹

Disposal of Sulfite Spent Liquor

Most sulfite pulp mills do not utilize the spent cooking liquor but instead dispose of it as a waste product. In these mills, approximately 50% of the wood is wasted and about 2,500 gal. of waste liquor at a solids content of about 10 to 12% are discharged into near-by streams for each ton of pulp produced. This is a highly undesirable situation from the standpoint of both economic waste and stream pollution. Public reaction against stream pollution and the need for greater economy in sulfite pulping is forcing the sulfite pulp industry to find efficient ways of utilizing waste products. Practically no attempts have been made to recover chemicals in those mills using calcium-base liquor, since the cost of chemical does not warrant

¹⁷⁰ E. R. Lang and E. T. Laurin, *Paper Trade J.* 116, No. 20: 227-230 (May 20, 1943)

¹⁷¹ F. H. Yorston, *Pulp Paper Mag. Canada* 48, No. 13: 74-80 (Dec., 1947)

the expense of recovery. There is, however, some interest in the recovery of heat and utilization of waste liquor by-products, as explained in the following sections. Where recovery of liquor is not practicable, attempts are being made to treat the spent liquor to reduce pollutional load on near-by streams.

Burning of Concentrated Sulfite Liquor for Heat

Considerable work has been done in Europe and in the United States on the utilization of sulfite waste liquor as a source of fuel for the pulp mill. The potential heat value of dried sulfite waste liquor is between 7,000 to 8,000 B.t.u./lb., which is approximately two-thirds that of industrial coal. Thus, the burning of sulfite waste liquor offers a promising source of heat to the pulp mill and a means whereby stream pollution can be drastically reduced. It is theoretically possible to obtain enough steam by burning the waste liquor to supply the steam requirements for the cooking operation.

A number of major obstacles have blocked the utilization of sulfite waste liquor as a source of fuel. The inability to obtain wash liquor sufficiently concentrated to get a net heat surplus from the evaporation and combustion of the liquor has been one of the problems. Sulfite liquor obtained from the blowpits normally contains 10 to 12% total solids, and this must be concentrated to 50% total solids or more in order to utilize the liquor as a fuel and even then, supplementary fuel may be required. Further concentration to 60 to 65% solids is necessary in order to be able to burn without additional fuel and maintain the same capacity as that obtained with coal.¹⁷² This requires large amounts of energy (steam). The most efficient washing for liquor to be subsequently evaporated and burned has been described by Butler¹⁷³ as that which gives a dry substance yield (ratio of dry substance in the reclaimed liquor to the dry substance available in the digester liquor) of 87% and a concentration ratio (ratio of concentration of solids in the reclaimed liquor to concentration of solids in undiluted liquor) of 0.89.

In addition to the high energy requirements for evaporation, there are other very serious drawbacks to the evaporation of sulfite waste liquor. These are the tendency of the liquor to corrode furnace equipment and the tendency to scale or encrust the heating surfaces in evaporators. The introduction of stainless steel equipment has reduced the corroding effect of the sulfur in the liquor, and newer methods of handling have reduced the encrusting effect of the liquor. Encrustation is caused by the precipitation of calcium sulfate when the liquor is heated at high temperature due to the inverted solubility curve shown by calcium sulfate. Calcium sulfate tends to form supersaturated solutions in sulfite waste liquor, e.g., sulfite waste liq-

¹⁷² C. Rosenblad, *Pulp Paper Mag. Canada* 51, No. 6: 85-94 (May, 1950)

¹⁷³ W. T. Butler, *Pulp Paper Mag. Canada* 50, No. 11: 108-121 (Oct., 1949)

liquor can keep in solution more than ten times the amount of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as pure water,¹⁷⁴ but despite its tendency to produce supersaturated solutions, precipitation generally occurs toward the end of the evaporation process. The original precipitated sulfate is converted into the hemi-hydrate at about 100° C. and to the more difficultly soluble anhydrite at about 127° C.¹⁷⁵ Encrustation can be fairly well controlled when the liquor is evaporated at 100 to 105° C. under vacuum, but the heat efficiency is low under these conditions, and consequently the process is not economical.¹⁷⁶

The problem of prevention and removal of scale during evaporation has received considerable attention in Sweden. Two general methods have been proposed. The first suggested method of keeping down encrustation involves the preheating of the liquor at elevated temperature before evaporating to precipitate out the calcium sulfate as a sludge. This sludge is then carried through the evaporators without causing serious encrustation.^{177, 178} The greatest precipitation occurs at a pH of 3.5.¹⁷⁹

The second method of overcoming encrustation is to remove the soluble calcium sulfate hydrate from the evaporator surface before the hydrate is converted into insoluble anhydrite. This is the basis of the Rosenblad process¹⁸⁰ which is in successful use in several Swedish plants. In this process, the liquor is evaporated to 50 to 55% solids in multiple-effect stainless steel evaporators and then is burned in a furnace. Encrustation is kept down by interchanging periodically (about every 8 hours or longer) the flows of liquor and steam in the channels of the heat exchanger to remove the scale before it becomes thick enough to interfere with evaporation.¹⁸¹ Analyzing the condensate for sulfite ions indicates when the heating surface is clean.

The Ramen process is another process suggested in Sweden. In this proposed process, scaling is minimized by employing high velocities in the evaporators and by preheating the liquor to precipitate most of the scale-forming substances. The original idea in the Ramen process was to evaporate to a solids of 40 to 50%, then spray dry in hot flue gases, and burn in the solid state. However, attempts at burning dry powder have failed on account of powder caking on the boiler tubes.¹⁸²

¹⁷⁴ O. Samuelson, *Svensk Papperstidn.* 49: 575-581 (1946)

¹⁷⁵ H. Elgee, D. Craig and J. K. Russell, *Pulp Paper Mag. Canada* 51, No. 3: 182-189, Convention Issue (1950)

¹⁷⁶ W. T. Butler, *Pulp Paper Mag. Canada* 50, No. 11: 108-121 (Oct., 1949)

¹⁷⁷ O. Samuelson, *Svensk Papperstidn.* 50: 239-244 (1947)

¹⁷⁸ O. Brauns, *Svensk Papperstidn.* 50: 61-62 (1947)

¹⁷⁹ O. Samuelson, *Svensk Papperstidn.* 52, No. 11: 283-289 (June 15, 1949)

¹⁸⁰ F. W. Grewin and S. G. Lindberg, U. S. 2,490,750 (Dec. 6, 1949)

¹⁸¹ C. Rosenblad, *Pulp Paper Mag. Canada* 51, No. 6: 85-94 (May, 1950)

¹⁸² "Special Report on Evaporation and Burning of Calcium Base Sulfite Liquor in Scandinavia," *Paper Trade J.* 130, No. 1: 19-20, 22 (Jan. 5, 1950)

Recovery of Soluble-Base Spent Liquors

Of all the bases which might be employed in the sulfite process, magnesium lends itself most readily to chemical recovery, owing principally to the tendency of the magnesium sulfate in evaporated liquor to decompose on heating into magnesium oxide and sulfur dioxide, instead of being reduced to magnesium sulfide. Waste liquor containing magnesium base has some tendency to scale during evaporation, but this is not nearly so bad as it is in the evaporation of calcium-base liquor. The recovery of magnesium-base liquor is covered by patents.¹⁸³⁻¹⁸⁶

Recovery of magnesium-base liquor is carried out in a cyclic process in which waste liquor (about 12 to 14% solids) is collected and neutralized to pH 7 to 8 with recovered magnesium oxide to prevent loss of loosely held sulfur dioxide during the following evaporation. The liquor is evaporated in multiple-effect stainless steel evaporators to a solids content of 50 to 55%. In the original installation the liquor was then evaporated with hot gases in a cascade evaporator to a solids content of about 60 to 70%, but this caused trouble with foam and scale and later this type of evaporator was eliminated as a final stage. The concentrated liquor is burned in a recovery furnace where the magnesium salt is converted into magnesium oxide, which is carried off in suspended form in the flue gases and collected in a series of cyclonic separators. The burning is carried out at low temperatures to prevent conversion of magnesium oxide into the inactive (periclase) form. During burning, sulfur dioxide passes off in the flue gases and these gases are cooled and saved. About 8,000 lb. of steam are produced per ton of pulp.¹⁸⁷

In the final stage of the recovery, the recovered magnesium oxide (in the form of a slurry) is fed downward through a series of large gas absorption towers while the cooled flue gases (containing about 1% of sulfur dioxide) are allowed to rise through the towers. In this way, the recovered magnesia and sulfur dioxide are converted into magnesium bisulfite for reuse as cooking liquor. Excess oxygen in the air going to the gas absorption towers is held to a minimum to reduce the formation of magnesium sulfate. The pH is controlled between 4 to 5 to remove calcium from the system and to keep the concentration of magnesium monosulfite within the limits of 0 to 0.5%.¹⁸⁸ Recovery is claimed to be 75 to 88% of the mag-

¹⁸³ G. H. Tomlinson, U. S. 2,285,876 (June 9, 1942)

¹⁸⁴ G. H. Tomlinson, U. S. 2,238,456 (Apr. 15, 1941)

¹⁸⁵ G. H. Tomlinson, U. S. 2,385,955 (Oct. 2, 1945)

¹⁸⁶ R. S. Hatch, U. S. 2,308,364 (Jan. 12, 1943)

¹⁸⁷ G. H. Tomlinson and L. S. Wilcoxson, *Pulp Paper Mag. Canada* 41: 391 (1940)

¹⁸⁸ R. E. Baker and F. Hutton, *Pulp Paper Mag. Canada* 51, No. 6: 82-84 (May 1950)

nesium oxide and 65 to 70% of the sulfur.^{188, 189} Total make-up is about 20 to 50 lb. of magnesium oxide and about 70 to 100 lb. of sulfur per ton of pulp. Regular sulfur burner gas can be used for make-up of the sulfur loss and for fortification of the liquor. Advantages of the process, aside from the advantage of chemical recovery, are (1) the recovery of heat from burning of the concentrated liquor in self-sustaining combustion furnaces and (2) the reduction of stream pollution problems.

Recovery of chemical is somewhat more difficult with soda base than with magnesium base, because sulfur trioxide, as well as sulfur dioxide, is produced in combustion. The smelt contains sodium sulfide and sodium sulfate. The sulfate is reducible to sulfide, so that it is possible to obtain the sulfur mostly in the form of sulfide. The recovered chemical could be readily used in a sulfate mill, but the main difficulty preventing reuse in a sulfite mill lies in converting sodium sulfide to sodium bisulfite, which so far has not been done on a commercial scale. Sodium bisulfite can be recovered directly, but the process is rather involved and is not commercially feasible.¹⁹⁰ Treatment of the smelt with sodium bicarbonate has been suggested to drive off the sulfur in the form of hydrogen sulfide, which can be burned with sulfur in the sulfur burner to produce sulfur dioxide for use in making fresh liquor.

No attempt has so far been made on the part of the mills using ammonia-base liquor to recover ammonia and sulfur. The most likely method of recovery appears to be one involving a pyrolysis of predried waste liquor at 500 to 600° C. under controlled conditions involving the admission of moist air. By treatment in this way, a high percentage of ammonia and sulfur in the form of sulfur dioxide can be recovered. However, the process is not commercially feasible at the present time.

Uses for Concentrated Sulfite Waste Liquor

The low solids of the wash liquors makes it uneconomical to ship unevaporated sulfite waste liquor any distance from the sulfite mill. On the other hand, the high cost and difficulties of evaporation make it difficult to find uses for concentrated liquor where it can compete economically with other materials. Partially evaporated sulfite waste liquor has been suggested for use as an adhesive, tanning agent, insecticide, oil well drilling compound, rubber compounding agent, ore flotation agent, fertilizer, road binder, emulsifying agent, and dispersing agent for cement, ceramics, drilling mud, and printing inks. For many of these purposes, however, the raw waste liquor is not sufficiently pure to be satisfactory.

¹⁸⁹ S. E. Hazelquist and C. E. Rogers, *Pulp and Paper* 24, No. 7: 39, 102-108 (June, 1950)

¹⁹⁰ P. S. Billington, G. H. Chidester and C. E. Curran, *Paper Trade J.* 1, No. 11: 140-146 (Sept. 12, 1935)

The solids in waste sulfite liquor are composed of about 15 to 20% sugars, 10 to 15% incompletely hydrolyzed carbohydrates, 60% lignosulfonic acids, and 10% of calcium sulfate, calcium bisulfite, acids, methanol, and other minor ingredients. The calcium lignosulfonic acids themselves are polydisperse, ranging in molecular weight from about 2,000 to 18,000 the majority having a molecular weight of 10,000 or more. Lignosulfonic acids are conventionally divided into alpha and beta acids, depending upon the ease of precipitation. The alpha lignosulfonic acids are precipitated by the addition of aromatic amines (e.g., beta-naphthylamine hydrochloride or quinoline). The beta lignosulfonic acids are not precipitated with aromatic amines, but are precipitated with basic lead acetate. The beta acid appears to be formed from the alpha acid at high temperatures.¹⁹¹ Recent evidence indicates that there is a gradual transition in compounds, rather than any sharp distinction. Precipitation with beta-naphthylamine hydrochloride is sometimes used to determine the total lignin content of sulfite waste liquor. Since this reagent precipitates only about 82% of the lignosulfonic acids in the liquor, it is necessary to multiply the weight of precipitate by the factor 1.22 to obtain the total weight of lignin in the liquor.

Because of difficulties in finding commercial uses for such a complex mixture of compounds as that found in sulfite waste liquor, attempts have been made to separate relatively pure lignosulfonic acids. Some of these methods are interesting from a laboratory standpoint, although most processes are not practical from an industrial standpoint. One method of removing sugars which is practiced commercially is by fermentation into alcohol. Another method, not practical commercially, for removing sugars and inorganic reagents is dialysis.¹⁹² The use of ion exchange resins has afforded a rapid and convenient means of separating the individual constituents of sulfite waste liquor in the laboratory. Cations can be removed by passing the dilute liquor over a cation exchange resin. Acids of low molecular weight (sulfuric, sulfurous, and acetic acids) can be removed by passing the liquor over anion exchange resins, thereby producing a solution containing principally carbohydrates and lignosulfonic acids.¹⁹³⁻¹⁹⁵ Special anion exchange resins can be used for removing sugars from the de-acidified liquor.¹⁹⁶

¹⁹¹ E. Hägglund, *Svensk Kem. Tid.* 42: 159 (1930)

¹⁹² N. K. Hiester, J. L. McCarthy and H. K. Benson, *Paper Trade J.* 126, No. 16: 202-205 (Apr. 15, 1948)

¹⁹³ O. Samuelson and A. Westlin, *Svensk Papperstidn.* 51, No. 8: 179 (Apr. 30, 1948)

¹⁹⁴ L. Stockman and E. Hägglund, *Svensk Papperstidn.* 51, No. 12: 269-274 (June 30, 1948)

¹⁹⁵ F. H. Yorston, *Pulp Paper Mag. Canada* 50, No. 12: 108-111 (Nov., 1949)

¹⁹⁶ F. H. Yorston, *Pulp Paper Mag. Canada* 50, No. 12: 111-113 (Nov., 1949)

It is possible to evaporate calcium lignosulfonic acids to the solid state, but there are many difficulties, which have already been mentioned. In addition to the difficulties of evaporation, there is the difficulty in drying calcium lignosulfonic acids, because the acids tend to decompose at high temperatures with the formation of sulfur dioxide, calcium sulfite, calcium sulfate, and some sulfur trioxide.¹⁹⁷⁻²⁰⁰ Because of the difficulties involved, evaporation of solid lignosulfonic acids has not been regarded with much favor as a commercial process.

Precipitation of Lignosulfonic Acids

A number of processes for the precipitation of lignin solids from sulfite waste liquor have been proposed. Some of the precipitants which have been suggested are lime, sulfuric acid, calcium chloride, basic lead acetate, barium salts, organic bases, and phenols, but so far, the only process in commercial use is the Marathon-Howard process using lime, which is described below.

The Marathon-Howard process²⁰¹⁻²⁰⁵ is based upon the fractional treatment of sulfite liquor involving the controlled addition of lime in three stages. In the first stage, the liquor is treated at 9% solids at a temperature of 70° C. with about 1 lb. lime per gallon (*pH* 10.5) whereupon calcium bisulfite, loosely bound sulfur, and a small amount of lignin are precipitated. The recovered calcium monosulfite is returned to the sulfite mill and reused in the preparation of fresh cooking acid. About 60 to 75 lb. of sulfur and 100 to 130 lb. of lime are recovered per ton of pulp in this stage. In the second stage, the liquor is again treated with lime (*pH* 11.0), whereupon a yellow organic precipitate is obtained which consists mostly of basic calcium lignosulfonate. This is continuously separated on a rotary vacuum filter as a filter cake of 30 to 35% solids. About 1,000 to 1,200 lb. of basic calcium lignosulfonate is recovered, or about 60 to 80% of the lignin originally present in the liquor. The yield of lignin product per ton of dry pulp is slightly higher for hemlock than for spruce. In the third stage, more lime is added to precipitate additional lignin. The liquor from this third stage contains considerable amounts of unreacted lime and is used as the pre-

¹⁹⁷ O. Samuelson and A. Westlin, *Svensk Papperstidn.* 51, No. 8: 179-185 (Apr. 30, 1948)

¹⁹⁹ O. Samuelson, *Svensk Papperstidn.* 50: 239 (1947)

²⁰⁰ J. M. Pepper, *Pulp Paper Mag. Canada* 46, No. 2: 83-91 (Feb., 1945)

²⁰¹ G. Howard, *Paper Trade J.* 103, No. 1: 84 (July 2, 1936)

²⁰² G. C. Howard, U. S. Pat. Reissue 18,268 (Dec. 1, 1931)

²⁰³ G. C. Howard, U. S. 1,856,558 (May 3, 1932)

²⁰⁴ L. T. Sandborn, J. R. Salvesen and G. C. Howard, U. S. 2,057,117 (Oct. 13, 1936)

²⁰⁵ L. T. Sandborn, U. S. 2,104,701 (Jan. 4, 1938)

precipitating liquor in the first stage. The effluent has a B.O.D. only about one-third that of the original liquor.

The lignin product has been suggested for many uses. In the Marathon plant, part of the lignin has been used for manufacturing vanillin, and part for impregnating fibrous molding compound. An important use has been as a fuel, in which case the filter cake is pressed to 50% solids and burned in combination with coal. The fuel value is 8,000 to 8,500 B.t.u. per pound of dry solids. Names of some of the commercial lignosulfonates obtained from waste sulfite liquor are Binderene (International Paper Company), Goulac and Glutrin (Robeson Process Company), and Maraspers and Maratex (Marathon Corporation).

Chemical Derivatives from Sulfite Waste Liquor

A promising possibility for sulfite waste liquor lies in its use as a raw material for the manufacture of various chemical derivatives. A vast amount of work remains to be done in this field.

One of the important by-products produced from sulfite waste liquor is vanillin. Vanillin manufacture is not a large business, since the waste liquor from one large sulfite mill is sufficient to supply all the vanillin required in the United States, but it serves as an interesting example of by-product use.

Vanillin is produced by the alkaline hydrolysis of basic calcium lignosulfonate (Marathon-Howard process) or by the alkaline hydrolysis of concentrated sulfite waste liquor (Howard Smith process). In both processes, hydrolysis is carried out in the presence of strong caustic soda solution at high pressure and temperatures in the neighborhood of 160° C.²⁰⁶⁻²¹⁰ The resultant solution contains the sodium salt of vanillin, and this can be extracted directly from the alkaline solution with butanol (Marathon-Howard process) or the vanillin can be precipitated with carbon dioxide and extracted with benzene (Howard Smith process).²¹¹ In the Marathon-Howard process, after removal of the butanol, the residual water solution is acidified with sulfur dioxide to precipitate and remove the impurities, after which sulfuric acid is added to liberate the vanillin. The crude vanillin obtained by these processes is subjected to distillation at high vacuum followed by recrystallization from water. The maximum attainable yield of vanillin by alkaline hydrolysis is about 6 to 7% of the total lignin derivatives,^{212, 213} but the commercial yield is about 2 to 3%.²¹⁰ The yield of vanil-

²⁰⁶ L. T. Sandborn, J. R. Salverson and G. C. Howard, U. S. 2,057,117 (Oct. 13, 1936)

²⁰⁷ L. T. Sandborn, U. S. 2,104,701 (Jan. 4, 1938)

²⁰⁸ H. Hibbert and G. H. Tomlinson, U. S. 2,069,185 (Jan. 26, 1937)

²⁰⁹ R. S. Hatch, U. S. 2,099,014 (Nov. 16, 1937)

²¹⁰ I. A. Pearl, *Tappi* 33, No. 6: 263-267 (June, 1950)

²¹¹ G. H. Tomlinson, *Chemistry & Industry* 57: 1047 (1938)

lin is higher the higher the sulfur content of the lignosulfonic acids.^{212, 214} Yield can be increased by introducing gaseous oxygen under pressure,²¹⁵ or by oxidation with mild alkaline oxidizing agents.²¹⁶ Only softwood lignins are suitable, since hardwood lignins produce a high percentage of syringaldehyde, together with vanillin. Esters of vanillic acid (e.g., ethyl vanillate) have been proposed as preservatives for foodstuffs.

Sulfite waste liquor has been utilized, particularly in Europe, for the production of alcohols, fodder yeasts, and organic acids. The principal fermentable sugars are hexoses (glucose and mannose), and hence waste liquor from softwoods is preferred. In making alcohol, the sulfur dioxide must first be removed from the waste liquor by steam stripping.²¹⁷ The liquor is then cooled, adjusted to a pH of about 5.0 with lime, certain missing food elements added (e.g., nitrogen and phosphate compounds), and the treated liquor is fermented with yeast in special fermenters. The liquor may be pumped from fermenter to fermenter with as many as seven fermenters being used. After fermentation, the yeast is removed in separators and the beer, which contains about 1% ethyl alcohol by volume, is evaporated in stills.²¹⁸ The alcohol is finally heated at 40 lb. pressure to destroy impurities and is then rectified to 95% by volume. The yield of alcohol (ethanol) is generally about 20 gal. per ton of pulp, although yields as high as 35 gal. per ton have been obtained. The alcohol produced must compete with that made from the fermentation of blackstrap molasses or grain and that made by synthesis from petroleum (ethylene), which in general are cheaper processes. Consequently, the production of alcohol from sulfite waste liquor is not extremely attractive, although one Canadian and one American mill are producing alcohol. Experiments are being conducted to improve the process along such lines as developing special strains of yeast particularly suited for growth in sulfite waste liquors. Using sulfite waste liquor for alcohol production does not eliminate the disposal problem, since the fermentation residues are nearly as objectionable as the original liquor. In addition to alcohol production, sulfite waste liquor can be fermented with varieties of *Clostridium* to yield butanol, butyric acid, and acetone,^{219, 220} but so far these processes have not proved commercially feasible.

²¹² G. H. Tomlinson and H. Hibbert, *J. Am. Chem. Soc.* 58: 345-348 (1936)

²¹³ O. Alvfeldt and E. Hägglund, *Svensk Papperstidn.* 40: 237-238 (1937)

²¹⁴ O. Alvfeldt and E. Hägglund, *Svensk Papperstidn.* 40: 237-238 (1937)

²¹⁵ J. R. Salvesen, D. L. Brink, G. D. Diddams and R. Orozarski, U. S. 2,434,626 (Jan. 13, 1948)

²¹⁶ J. A. F. Gardner, *Pulp Paper Mag. Canada* 50, No. 9: 102-104 (Aug., 1949)

²¹⁷ R. H. McKee, *Pulp Paper Mag. Canada* 18: 715-718 (1920)

²¹⁸ *Pulp and Paper* 23, No. 9: 44-51 (Aug., 1949)

²¹⁹ F. H. Yorston, *Dominion Forest Service Bull.* 97, Canadian Dept. of Mines and Resources, Ottawa (1942)

²²⁰ W. B. Beazley, H. W. Johnston and O. Maass, *Dominion Forest Service Bull.* 95, Canadian Dept. of Mines and Resources, Ottawa (1939)

Sulfite waste liquor is suitable for the growth of certain yeasts, such as *Torula utilis* and *Saccharomyces cerevisiae* (bakers' yeast). These yeasts make excellent supplementary feed for poultry, horses, hogs, and other livestock because of the high protein content, which is over 40% in the case of *Torula utilis*. Both the fermentable and non-fermentable sugar in the liquor are utilized so that the oxygen demand of the liquor is reduced by approximately 50 to 60%, thus making possible a great reduction in stream pollution.

Other Uses for Lignosulfonic Acids

It is known that calcium lignosulfonate acts as a specific dispersing agent which improves the strength, workability, and watertightness of cement. However, the product must be relatively pure, since sugar adversely affects the properties of the cement.²²¹

Salts of lignosulfonic acids have been suggested for use as tanning agents. In order to obtain a satisfactory product, however, it is necessary to remove calcium, sulfur dioxide, iron, and carbohydrates, and to treat the residue with sulfuric acid to convert the organic salts to lignosulfonic acids and react to produce sodium or ammonium salts which act as the tanning agent. Combined lime can be removed by treating the waste liquor solids with aluminum sulfate, ferric sulfate, oxalic acid, lactic acid, or similar material. Carbohydrates can be removed by fermentation. Improved tanning agents are obtained by condensing the lignosulfonic acids with hydroxy aromatic compounds using processes of which most are patented. Even under the best circumstances, however, tanning agents obtained from sulfite waste liquor are considered inferior to natural vegetable tannins and are generally used in mixture with the natural tannins. Purified lignosulfonic acids can be used as ion exchange resins.

Another use for lignosulfonic acids has been in the plastics field, although in general the quality of the plastics produced with 100% ligneous material is poor. Under certain conditions, lignins can be used as a thermoplastic binder to replace one-half of the phenol fraction in phenol-formaldehyde molding powders with only slightly decreased strength and water absorption.²²² The residual alkaline liquor obtained as a by-product from vanillin manufacture in the Marathon process has been used in this way. A "plastic pulp" suitable for molding can be obtained by cooking wood in the presence of sulfite waste liquor and precipitating the lignosulfonic acids onto the chips.^{223, 224}

²²¹ E. W. Scripture, *Paper Trade J.* 129, No. 17: 414-418 (Oct. 27, 1949)

²²² M. Plunguian, *Ind. Eng. Chem.* 32: 1399 (1940)

²²³ J. G. Meiler, *Modern Plastics* 64 (Sept., 1942)

²²⁴ H. Schwartz, *Pulp Paper Mag. Canada* 45, No. 9: 675-677 (Aug., 1944)

ALKALINE PULPING

The two principal alkaline processes used for the pulping of wood are the soda and the sulfate processes. In both processes, sodium hydroxide is present as the major cooking chemical, and in the sulfate process, sodium sulfide is also present. In one sense, a pure soda cook can be considered as a sulfate cook of zero sulfide content (zero sulfidity). However, most soda mills use a small amount of sulfur in the cooking liquor (sulfidity about 5%) and hence are really cooking by a modified soda process.

The sulfate process is a newer process than the soda process, having been invented by Dahl, a German chemist, in 1889. It is similar to the soda process except that the alkali which is lost in the process is replaced with sodium sulfate instead of sodium carbonate. During the alkali recovery process, this sulfate is reduced to sulfide. The term "sulfate" is therefore misleading, since it implies that sulfate is the active cooking agent, whereas it is actually sodium hydroxide and sodium sulfide. The sulfate process is used to produce pulps which vary from dark-colored pulps to soft, easy bleaching pulps. The kraft process is a variation of the regular sulfate process in which the pulp is intentionally undercooked to produce dark-colored pulp of exceptional strength. Kraft is taken from the German and means "strong." The sulfate process is superior to the soda process in pulp yield, pulp quality, and cost of production. It has grown very rapidly, whereas soda pulp production has been maintained at a fairly constant level. There is, however, considerable similarity in the soda and sulfate processes, and for this reason they are discussed together in the following sections.

Alkaline pulping is carried out in welded steel digesters, usually without lining. The digesters may be heated with either direct or indirect steam and, in some cases, an outside liquor circulating system is used. Most of the newer sulfate mills have positive circulation and indirect heating of the liquor using heat exchangers made from stainless metal. Direct heating is sometimes used when making raw pulps by a quick cook. The advantages of forced circulation and indirect heating are lowered steam costs through return of condensate to boilers, lower liquor volumes, and greater uniformity of cooking. Some of the other engineering improvements in the sulfate process are use of chip packers to increase digester capacity, digester blow-down recovery systems to utilize waste heat, and electrical precipitators on the stacks to remove the solids in the stack gases. A flow chart of a typical sulfate mill is given in Figure IV-11.

Terms Used in Alkaline Pulping

The generally accepted terms used in alkaline pulping are given below. Sulfate liquors are generally more complicated than soda liquors because of the presence of the sodium sulfide.

- (1) *Total chemical.* Total chemical is the concentration of all the sodium salts, expressed as Na_2O .
- (2) *Total alkali.* In the soda process, total alkali includes NaOH plus Na_2CO_3 . In the sulfate process, this includes $\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$. Total alkali should be expressed as Na_2O , although some of the older soda mills express as Na_2CO_3 or NaOH .
- (3) *Total titratable alkali.* In the soda process, total titratable alkali is the same as the total alkali. In the sulfate process, it includes $\text{NaOH} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{S}$, all expressed as Na_2O .
- (4) *Active alkali.* In the soda process, active alkali includes only the NaOH , expressed as Na_2O . In the sulfate process, this includes $\text{NaOH} + \text{Na}_2\text{S}$, expressed as Na_2O .
- (5) *Activity.* Activity is a percentage found by dividing active alkali by total titratable alkali.
- (6) *Causticizing efficiency.* Causticizing efficiency is a percentage found by dividing NaOH by $\text{NaOH} + \text{Na}_2\text{CO}_3$, both items being expressed as Na_2O .
- (7) *Causticity.* Causticity is a percentage found by dividing NaOH , expressed as Na_2O , by total titratable alkali. In the soda process, causticity, activity, and causticizing efficiency are the same.
- (8) *Sulfidity.* Sulfidity is a term used in the sulfate process. It is a percentage found by dividing Na_2S , expressed as Na_2O , by total titratable alkali (in some cases by dividing by $\text{Na}_2\text{S} + \text{NaOH}$).
- (9) *Reduction.* Reduction is a term used in the sulfate process. It is a percentage based on the analysis of green liquor and obtained by dividing Na_2S by $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}$, all expressed as Na_2O .
- (10) *Unreduced salt cake.* Reduction is a term used in the sulfate process. It gives the concentration of Na_2SO_4 in the green liquor, expressed as Na_2SO_4 in grams per liter.
- (11) *Chemical consumption.* In the soda process, chemical consumption is the pounds of Na_2CO_3 added per day, divided by the tons of air-dry pulp produced per day. In the sulfate process, it is the Na_2SO_4 added per day divided by the tons of air-dry pulp produced per day.
- (12) *Chemical recovery.* In the soda process, chemical recovery is a percentage found by dividing the total alkali to the digesters less the sodium carbonate (expressed Na_2O) in new chemical by the total alkali to the digesters after correcting for any change in the liquor inventory. Chemical recovery is calculated the same for the sulfate process, except that sodium sulfate instead of sodium carbonate is used.
- (13) *Chemical loss.* The chemical loss sustained in alkaline pulping can be expressed as follows. All items should be corrected for any change in liquor inventory. (a) *Total:* A percentage found by dividing sodium carbonate (soda process) or sodium sulfate (sulfate process) in the new chemical by total alkali to the digesters, all expressed as Na_2O . (b) *Loss in pulp washing:* A percentage found by dividing the total alkali to the digesters, less the total alkali to the evaporators, by the total alkali to the digesters. (c) *Loss in evaporators and furnace:* A percentage found by dividing the total alkali to the evaporators (plus sodium sulfate added as new chemical to the sulfate process) minus total alkali in the green liquor by the total alkali to the digesters. (d) *Loss in recausticizing and mud washing:* A percentage found by dividing the total alkali in the green liquor, minus the total alkali in the white liquor, by the total alkali to the digesters.
- (14) *Green liquor.* The name applied to liquor made by dissolving the recovered chemicals in water and weak liquor preparatory to causticizing.

(15) *White liquor*. The name applied to liquors made by causticizing green liquors. White liquors are ready for use in the digester.

(16) *Black liquor*. The name applied to liquors recovered from the digesters up to the point of their incineration in the recovery plant.

In reporting laboratory data, the Na_2O content of the liquor should be expressed in grams, while in reporting mill operations, the Na_2O is best expressed in pounds. When expressing concentrations, grams per liter is preferred for laboratory work, whereas pounds per cubic foot is recommended for mill reports. All articles written for publication should clearly state which basis is used in order that the reader may be able to calculate to any comparison preferred. In calculations based upon green liquor, the analysis should be corrected for the content of the weak liquor usually used in dissolving the smelt.²²⁵

The important analytical tests customarily made on soda digestion liquor are total alkali, sodium hydroxide, and sodium carbonate. These determinations may be carried out as described below.

Total alkali may be determined by acidifying a sample of the diluted liquor with a definite volume of 0.5 *N* hydrochloric acid, boiling to expel carbon dioxide, and titrating the excess acid with 0.1 *N* sodium hydroxide using methyl red indicator. By subtracting one-fifth of the number of milliliters of 0.1 *N* base from the number of milliliters of 0.5 *N* acid used, the amount of 0.5 *N* acid required to neutralize the total alkalinity is obtained.

$$1 \text{ ml. } 0.5 \text{ } N \text{ acid} = 0.01550 \text{ g. sodium oxide}$$

The amount of sodium hydroxide in soda liquor may be determined by adding barium chloride solution to the liquor to precipitate the sodium carbonate and then titrating the clear solution with 0.5 *N* acid, using phenolphthalein as the indicator.

$$1 \text{ ml. } 0.5 \text{ } N \text{ acid} = 0.2000 \text{ g. sodium hydroxide}$$

The sodium carbonate content can be determined by subtracting the amount of 0.5 *N* acid used for the sodium hydroxide determination from the amount of 0.5 *N* acid used in the total alkali determination.

$$1 \text{ ml. } 0.5 \text{ } N \text{ acid} = 0.02650 \text{ g. sodium carbonate}$$

It is also possible to determine the amount of carbonate and hydroxide by double titration with 0.5 *N* acid, using phenolphthalein and methyl orange as the two indicators. This method is more widely used than the above for mill control work. It is possible to use the burette readings directly for calculating causticity. The first titration (phenolphthalein end point) neutralizes all the hydroxide and half of the carbonate. The total titration (methyl orange end point) gives the total alkalinity. From this, the hydroxide and carbonate can be calculated as follows:

$$\text{Milliliters of acid due to carbonate} = 2 (\text{second titration} - \text{first titration})$$

$$\text{Milliliters of acid due to hydroxide} = \text{second titration} - \text{milliliters acid due to carbonate}$$

The principal chemical tests made on sulfate digestion liquor are for sodium sulfate, total alkali, active alkali, total reducing agents, and sodium sulfite plus sodium thiosulfate. From these determinations, it is possible to calculate the amount of sodium hydroxide, sodium carbonate, sodium sulfate and sodium sulfite in the liquor. The methods are described briefly below.

²²⁵ Taken from TAPPI Standards

Sodium sulfate is determined as follows. A 25-ml. sample of the liquor is diluted, neutralized with an excess of hydrochloric acid and evaporated, after which the residue is filtered. The filtrate contains the sodium sulfate which is then precipitated by adding barium chloride to the boiling solution. The precipitated barium sulfate is collected on a filter paper, washed, ignited, cooled, and then weighed.

$$1 \text{ g. BaSO}_4 \times 0.6086 \times 40 = \text{grams of sodium sulfate per liter}$$

The total alkali is determined as follows. A 25-ml. sample of the liquor is diluted to 500 ml., treated with furfural, and then a 50-ml. aliquot is titrated with 0.5 *N* hydrochloric acid, using methyl orange as the indicator. The acid fully neutralizes all the sodium hydroxide, sodium sulfide, sodium carbonate, and one-half of the sodium sulfate. Total alkali in grams per liter is calculated as the number of milliliters of 0.5 *N* HCl $\times 0.0155 \times 400$.

The active alkali (NaOH plus Na₂S) is determined by treating 25 ml. of liquor with barium chloride solution to precipitate the carbonate, sulfate, and sulfite, and (after diluting to 500 ml.) titrating 50 ml. of the supernatant solution with 0.5 *N* hydrochloric acid using methyl orange as the indicator. The active alkali in grams per liter is calculated as number of milliliters of 0.5 *N* HCl $\times 0.0155 \times 400$.

Sodium sulfide can be determined in several different ways. One method is to subtract the sodium sulfite plus sodium thiosulfate determination from the determination for total reducing agents (sulfide, sulfate, plus thiosulfate). Sodium sulfide can be determined directly by titrating with silver nitrate or by double titration with hydrochloric acid. The methods are briefly described below.

The total reducing agents (sulfide, sulfite, and thiosulfate) are determined by diluting 25 ml. of the liquor to 500 ml. and then titrating a 10-ml. aliquot with 0.1 *N* iodine after neutralizing with acetic acid and adding a few drops of starch indicator. The amount of iodine used is an indication of the total reducing agents.

In another sample, the sodium sulfide is precipitated with zinc salt (zinc carbonate or zinc acetate), and the filtrate is titrated with 0.5 *N* iodine to determine the amount of sulfite and thiosulfate present. The concentration of sodium sulfide can then be calculated by subtracting the last reading from the reading for the total reducing agents.

Sodium sulfide may be determined directly by diluting 25 ml. of the liquor and then titrating with standard ammonical silver nitrate.

For routine mill analysis where high accuracy is not required, sodium sulfide can be determined by double titration of the carbonate- and sulfite-free solution to phenolphthalein and methyl orange end points using 0.5 *N* hydrochloric acids. The amount of acid required between the two end points corresponds to the conversion of NaHS to H₂S. Sodium sulfide and sodium hydroxide can be calculated from the titration as follows, using *A* as the number of milliliters of acid to the phenolphthalein end point and *B* as the number of milliliters of acid to the methyl orange end point.

$$\begin{aligned}\text{Na}_2\text{S} &= 2(B - A) \times 0.0155 \\ \text{NaOH} &= 2A - B \times 0.0200\end{aligned}$$

The Borlew and Pascoe method²²⁶ is one of the simplest and most accurate methods of analyzing sulfate liquor. It is particularly well suited

²²⁶ P. B. Borlew and T. A. Pascoe, *Paper Trade J.* 125, No. 10: 99-102 (Mar. 7, 1946)

to the analysis of used or partially used liquor. Two titrations are involved, and these are discussed briefly below.

In the first titration, the liquor is treated with barium chloride and the supernatant liquid is then titrated with hydrochloric acid to pH levels of 11, 10, and 8.25 in a pH meter having a shielded high sodium glass electrode and a calomel electrode. This titration gives the total amount of free sodium hydroxide, plus one-half of the free sodium sulfide.

In the second titration, using a separate sample, the total free sodium sulfide is determined by titrating in a pH meter having a silver sulfide-silver electrode with 0.1 *N* silver nitrate after the sample has been prepared by adding sodium hydroxide and ammonium hydroxide in such amounts that the final solution is 1 *N* in sodium hydroxide and 0.05 *N* in ammonium hydroxide. The end point of the titration is indicated by a sharp drop in the millivolt reading.

Variables in Alkaline Pulping

For a given digester charge, there are five important variables in alkaline pulping: composition of cooking liquor (i.e., sulfidity), concentration of cooking liquor, chemical-to-wood ratio, temperature, and time of cooking. Concentration bears a relationship to per cent active chemical on wood weight and ratio of cooking liquor to wood weight. Fixing any two of these factors automatically fixes the remaining one (unlike the sulfite process) and consequently, only two of these factors need be specified for establishing the cooking conditions.

Penetration of alkaline cooking liquors into the wood chips is quite different from the penetration of sulfite liquor. Penetration with alkaline cooking liquor is approximately the same in all directions of the chip,²²⁷ because sodium hydroxide is able to pass through the cell walls, whereas neutral and acid solutions must depend largely on longitudinal diffusion through the tracheids.²²⁸ The large transverse diffusion occurring with alkaline liquids is believed to be due to swelling which opens up the cell wall structure. The result is that alkaline liquors penetrate wood more rapidly than acid sulfite liquor, and hence penetration is less of a problem in the soda and sulfate process than it is in the sulfite process. The length of the chip in the fiber direction is not as much of a factor as it is in sulfite cooking, although it is important to have chips of uniform length, and generally speaking, the average length of the chips used in the sulfate process is from $\frac{1}{2}$ to $\frac{3}{4}$ in.

In alkaline pulping, spent liquor is often used as part of the cooking liquor for the following reasons:²²⁹ (1) to dilute the white liquor, which is

²²⁷ G. L. Larocque and O. Maass, *Can. J. Research* 15, Section B, No. 3: 89-97 (Mar., 1937)

²²⁸ W. B. Beazley, H. W. Johnston and O. Maass, *Dominion Forest Service Bull.* 95, Canadian Dept. of Mines and Resources, Ottawa (1939)

²²⁹ G. F. Allo, *Pulp Paper Mag. Canada* 47: 116-118, Convention Issue (1946)

usually made up stronger than needed; (2) to save chemicals without costly evaporation; (3) to utilize the heat in the waste liquor; (4) to aid in penetration. In some instances, up to 50% of the cooking liquor can be spent (black) liquor without affecting the rate of cooking, yield, and strength of the pulp. Generally, this much black liquor lowers the color of the pulp,²³⁰ although it has been reported in one case²³¹ that sulfate pulps of lowest permanganate number were obtained at 60% use of black liquor. Typical cooking conditions for the sulfate process for both a kraft and a bleachable grade of sulfate pulp are given in Table IX.

TABLE IX
COOKING CONDITIONS IN SULFATE PROCESS

	Kraft cook	Bleachable sulfate cook
Per cent active chemicals on O.D. wood (NaOH + Na ₂ S as Na ₂ O)	15-18%	24-28%
Concentration of active chemicals (NaOH + Na ₂ S as Na ₂ O)	50 g./l.	60 g./l.
Approximate sulfidity	20-30%	20-30%

Effect of Chemical-to-Wood Ratio in Alkaline Pulping

In commercial pulping by the soda process, about 18 to 35% sodium hydroxide is used on the weight of the wood. In the sulfate process, as generally practiced in the United States, the total active chemical expressed as Na₂O is 15 to 28% of the wood weight and, in some cases, up to 30% or higher. In making coarse kraft pulps for corrugating material, insulation, or paperboard where the cook is carried out to obtain a high yield, a low per cent of active alkali is used, and the pulp is blown when coarse and "woody," after which the stock from the blow tank is refined in disk refiners in the presence of hot black liquor. Kraft pulps in yield as high as 62 to 64% have been prepared in this way, compared to a yield of 44 to 48% for the usual grades of bleachable sulfate pulps. The chlorine number of these high-yield pulps is in the range of 16 to 19, and the chlorine consumption for bleaching is very high (17 to 20%) so that these high-yield pulps are useful under present economic conditions only for coarse, unbleached papers.

Some alkali must be present at all times during alkaline pulping. Insufficient chemical results in dark pulps which are difficult to bleach.²³² If

²³⁰ E. Hägglund and G. Schollin-Borg, *Papier-Fabr.* 30: 359-363 (1932)

²³¹ H. C. Crandall and G. F. Enderlein, *Paper Trade J.* 123, No. 2: 16-17 (July 11, 1946)

²³² M. W. Bray and J. S. Martin, *Paper Trade J.* 113, No. 25: 313-324 (Dec. 18, 1941)

the pH falls below about 9, the lignin becomes insolubilized,²³³ and the coloring matter becomes adsorbed on the fibers.²³⁴

In cooking longleaf pine by the sulfate process, Bray and coworkers²³⁵ obtained the maximum screened yield at 18 to 20% total chemical and an initial concentration of 50 g./l. (chemical less than 18–19% resulted in increased screenings). Less alkali is required with hardwoods. For example, Bray and Martin²³⁶ found in the case of sweetgum, that 17.5%

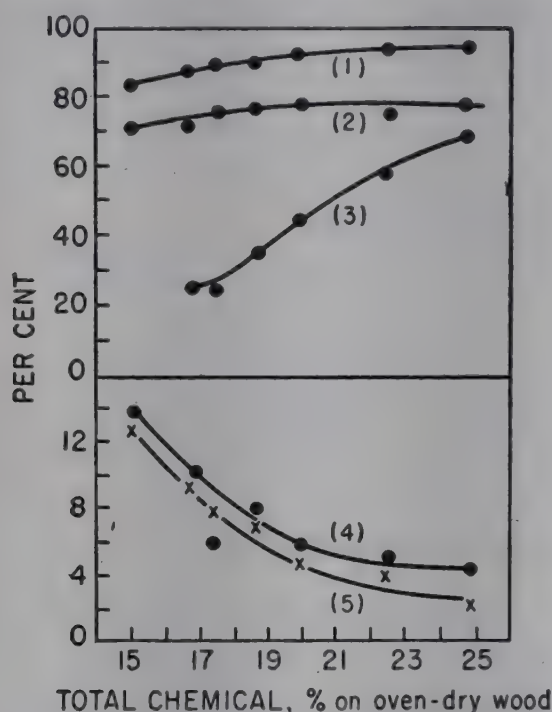


Fig. IV-12. Effect of chemical-to-wood ratio on properties of pulp produced from longleaf pine by the sulfate process: (1) total cellulose; (2) alpha cellulose; (3) degree of whiteness with 25% bleach; (4) chlorine number (Roe); (5) lignin content.

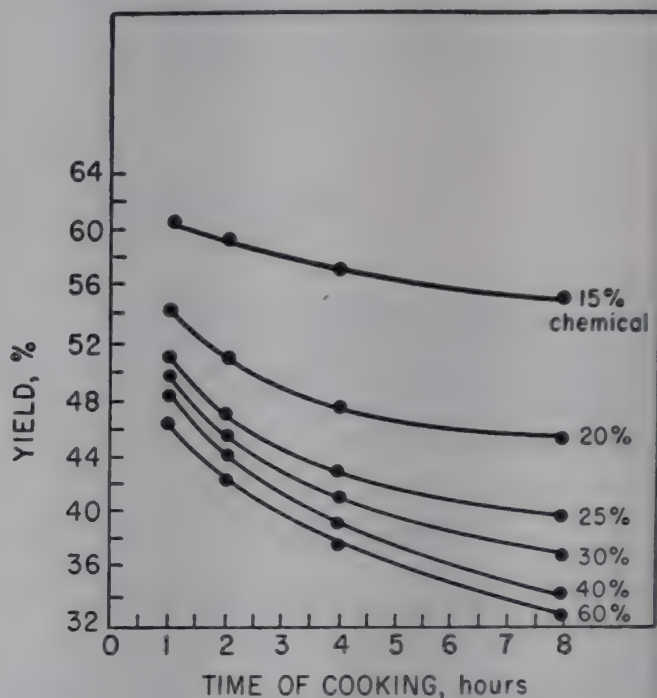


Fig. IV-13. Effect of time of cooking and per cent chemical on yield of Douglas fir cooked by the sulfate process.

chemical (Na_2O) was the optimum whereas 14 to 16% chemical has been reported as best for the pulping of scrub oak.²³⁷ Increasing the active chemical up to 25% decreases the yield slightly. Increasing it to 30% is highly wasteful and damaging to the fiber, tending to lower the alpha cellulose and

²³³ C. R. Mitchell and J. H. Ross, Forest Prod. Lab., *Can. Pulp and Paper Lab. Quarterly Rev.* 15: 7–11 (July, Sept., 1933)

²³⁴ M. W. Bray and J. S. Martin, *Paper Trade J.* 113, No. 25: 313–324 (Dec. 18, 1941)

²³⁵ M. W. Bray, J. S. Martin and S. L. Schwartz, *Paper Trade J.* 105, No. 24: 347–352 (Dec. 9, 1937)

²³⁶ M. W. Bray and J. S. Martin, *Paper Trade J.* 113, No. 25: 313–324 (Dec. 18, 1941)

²³⁷ R. L. Harvin, G. B. Hills, C. W. Rothrock and W. J. Nolan, *Tappi* 33, No. 7: 338–343 (July, 1950)

viscosity of the pulp, even if the yield is not affected.²³⁸ The effect of chemical-to-wood ratio on the properties of pine pulp is shown in Figure IV-12²³⁵ where it can be seen that the lignin content decreased while the brightness and cellulose content of the pulp increased as the total chemical was increased from 15 to 25%. Figure IV-13 shows the effect of per cent chemical on the yield of Douglas fir cooked by the sulfate process.²³⁸ The effects of the different cooking variables (per cent chemical, concentration of chemical, temperature, and cooking time) on the yield and lignin content of spruce cooked by the soda process are shown in Table X.²³⁹

TABLE X

EFFECT OF COOKING VARIABLES ON YIELD OF PULP AND PER CENT LIGNIN
IN PULP FOR SPRUCE COOKED IN SODIUM HYDROXIDE

NaOH on dry wood, %	Concn. of NaOH used, %	Tempera- ture, °C.	Cooking time, hours	Pulp yield, %	Lignin in pulp, %
15	3	160	1	70.8	29.9
20	3	160	1	69.5	29.4
25	3	160	1	68.0	28.4
15	3	180	1	64.0	25.8
20	3	180	1	58.0	21.0
25	3	180	1	53.7	18.3
15	5	160	1	70.8	28.7
20	5	160	1	68.2	27.0
25	5	160	1	64.0	25.5
15	5	180	1	59.8	23.2
20	5	180	1	50.6	15.2
25	5	180	1	47.3	10.8
15	4	180	3	59.7	25.9
20	4	180	3	46.8	11.5
25	4	180	3	44.0	6.3

The amount of alkali consumed by the wood in alkaline pulping generally varies from 15 to 18% of the weight of the wood. A consumption of 15% total chemical is necessary to affect defiberization of longleaf pine by the sulfate process.²⁴⁰ Increasing the chemical-to-wood ratio increases the total amount of alkali consumed, but the consumption based on total chemical added becomes less. For example, Bray and coworkers²⁴⁰ obtained a consumption of 93% at a chemical-to-wood ratio of 15%, whereas the con-

²³⁸ S. L. Schwartz and M. W. Bray, *Paper Trade J.* 107, No. 12: 141-148 (Sept. 22, 1938)

²³⁹ F. E. Brauns and W. S. Grimes, *Paper Trade J.* 108, No. 11: 136-139 (Mar. 16, 1939)

²⁴⁰ M. W. Bray, J. S. Martin and S. L. Schwartz, *Paper Trade J.* 105, No. 24: 347-352 (Dec. 9, 1937)

sumption was only 75% at a chemical-to-wood ratio of 25%. Figure IV-14 shows the relationship between the amount of wood dissolved and the amount of sodium hydroxide consumed in the soda process. These data were obtained by McCready and Nolan²⁴¹ based on previous work by Bray²⁴² and by Lewis and Laughlin.²⁴³ Schwartz and Bray²⁴⁴ found in the

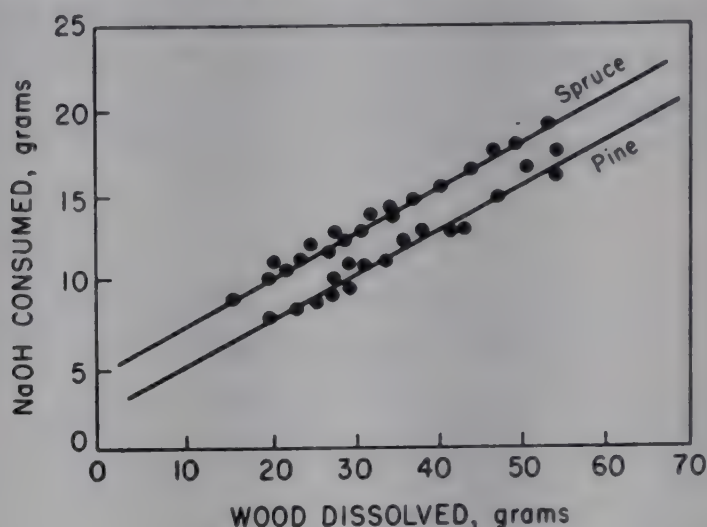


Fig. IV-14. Relationship between amount of wood dissolved and amount of sodium hydroxide consumed in the soda process.

pulping of Douglas fir by the sulfate process that increasing the ratio of chemical-to-wood increased the velocity of the reaction.

Effect of Liquor Concentration in Alkaline Pulping

The most important factor influencing alkaline pulping is the concentration of the cooking liquor. Ratio of chemical-to-wood is only a pseudo factor which, in combination with liquor ratio, serves to establish the concentration.

Increasing the concentration of chemical increases the rate of delignification and also effects a more rapid increase in the removal of cellulose.²⁴⁵ Bray and Curran²⁴⁶ found, when cooking with a constant alkali-to-wood ratio of 30%, that increasing the chemical concentration from 30 to 60 and again from 60 to 90 g./l. reduced the total cooking time required to obtain a pulp of constant yield by one-half. However, as the concentration of liquor is increased, the rate of attack on the cellulose is increased to a much greater extent than the attack on the lignin, with the result that the yield

²⁴¹ W. J. Nolan and D. W. McCready, *Paper Trade J.* 102, No. 4: 48-53 (Jan. 23, 1936)

²⁴² M. W. Bray, *Tech. Assoc. Papers* 12: 268 (1929)

²⁴³ H. F. Lewis and E. R. Laughlin, *Paper Trade J.* 91, No. 25: 259-262 (Dec. 18, 1930)

²⁴⁴ S. L. Schwartz and M. W. Bray, *Paper Trade J.* 107, No. 12: 140-148 (Sept. 22, 1938)

²⁴⁵ M. W. Bray and C. E. Curran, *Paper Trade J.* 97, No. 5: 30-35 (Aug. 3, 1933)

²⁴⁶ M. W. Bray and C. E. Curran, *Paper Trade J.* 97, No. 5: 52-57 (Aug. 3, 1933)

and strength are lowered and the bleach requirement is increased. At very high concentrations of chemical, the dissolution of non-ligneous materials passes through a maximum.²⁴⁷ Schwartz and Bray²⁴⁸ found that variations in the concentration of chemical in the cooking liquor from 70 to 100 g./l. have little effect on yield when cooking at a chemical-to-wood ratio of 15%. However, when cooking at a constant chemical-to-wood ratio of 30%, increasing the concentration of the cooking liquor lowered the yield and reduced the alpha cellulose content of the pulp, as shown in Table XI.^{246, 248} Thus, to obtain the maximum yield of cellulose at a given delignification and pulp yield, it is desirable to use liquors of relatively low concentration. Cooking at a high concentration of chemical should not be done when strong pulps of high alpha cellulose content are desired. There is, however, a practical limit beyond which the concentration cannot be reduced because of the necessity of completing the cook within a reasonable time.

TABLE XI

EFFECT OF INITIAL CONCENTRATION OF CHEMICAL IN SULFATE COOKING LIQUOR ON THE PULPING OF DOUGLAS FIR, USING 30% TOTAL CHEMICAL ON WEIGHT OF WOOD

Initial concn. cooking liquor, g./l.	Time of cooking, hours	Yield, %	Lignin, %	Cellulose, %	Alpha cellulose, %
40	4	43.49	1.3	99.1	84.2
60	4	41.20	1.0	98.0	82.0
80	4	40.45	1.1	98.6	82.8
100	4	39.04	0.9	98.5	81.1
120	2	42.02	1.2	97.5	78.2
120	4	37.42	1.3	99.0	70.2

In studying the effect of concentration of chemical in alkaline pulping, it should be kept in mind that the concentration automatically changes during the course of the reaction. The greatest change occurs in the early stages of cooking when a large part of the alkali is consumed in the neutralization of acidic substances derived from the hydrolysis of the wood components. If the cook is started with a low concentration of alkali, the decrease in concentration of free alkali is so rapid that the effect of the cooking agent is practically terminated early in the digestion.²⁴⁸ It is only when high initial concentrations are used that the full effect of liquor concentration is apparent. Liquors of comparatively low concentration would be sufficient for cooking if the concentration could be maintained at a constant value throughout the cooking cycle. One suggested method for maintain-

²⁴⁷ W. E. Adlington and J. H. Ross, *Pulp Paper Mag. Canada* 32: 248-251, 270 (1932)

²⁴⁸ S. L. Schwartz and M. W. Bray, *Paper Trade J.* 107, No. 12: 140-148 (Sept. 22, 1938)

ing more uniform concentration of alkali in the digester is injection cooking whereby the cook is started at low concentration of chemical and additional alkali is injected into the digester after the cook has been in progress for a period of time. Injection cooking of soda and sulfate pulps results in 10 to 20% higher strength, better color, and lower alkali consumption, compared to normal cooking.²⁴⁹⁻²⁵³ However, the process is not practiced to any extent commercially.

In commercial practice, about 50 to 60 g./l. of active chemical are used in alkaline pulping. The strength of the white liquor is ordinarily from 100 to 120 g. of alkali per liter expressed as Na_2O , but this is ordinarily diluted with black liquor, which establishes the limits of concentration indicated above. Liquor of greater than normal strength may be required in special cases, as, for example, when the wood is very wet. When cooking in indirectly heated digesters, more dilute solutions may be used than when the steam is admitted to the digester system directly. In commercial liquors there is always some sodium carbonate and a very small amount of calcium carbonate present in the liquor as a result of incomplete causticizing in the recovery plant. These other alkalies have no effect on the rate or nature of the reaction, provided there is sufficient sodium hydroxide present, although they do affect the properties of the final pulp.

There is a modern trend in sulfate pulping to use higher liquor-to-wood ratios at the same chemical application, particularly in the bleaching grades. The disadvantages of using high liquor ratios are high steam requirements in both cooking and recovery. Some of the sulfate mills are experimenting with the idea of cooking a very raw stock and then refining and purifying with large amounts of chlorine, thereby producing a pulp in very high yield.

Effect of Time and Temperature in Alkaline Pulping

The cooking cycle in alkaline pulping consists of three periods:²⁵⁴ (1) the pressure-raising and penetration period, (2) the full pressure period, (3) the pressure-reducing period. When hard kraft pulps suitable for container boards are being made, the third stage is sometimes eliminated and the digesters are blown as soon as full pressure is attained. In the regular sulfate process, the digester is relieved at intervals to reduce the false pressure caused by the volatile mercaptans and other gases which are given off.

²⁴⁹ J. N. Swartz, *Pulp Paper Mag. Canada* 47: 203-220, Convention Issue (1946)

²⁵⁰ S. D. Wells and K. A. Arnold, *Paper Trade J.* 113, No. 9: 103-106 (Aug. 28, 1941)

²⁵¹ S. D. Wells, G. E. Martin and D. R. Moltzau, *Paper Trade J.* 119, No. 19: 188-194 (Nov. 9, 1944)

²⁵² J. H. Ross, U. S. 1,922,622 (Aug. 15, 1933)

²⁵³ S. D. Wells, U. S. 1,649,669 (Mar. 4, 1934)

²⁵⁴ G. F. Allo, *Pulp Paper Mag. Canada* 47: 116-118, Convention Issue (1946)

It is important to relieve these gases, since they interfere with the delignification reaction. The relief is sometimes controlled automatically by pressure-temperature-time controllers.

Maximum pressure used in the sulfate process varies from 100 to 140 p.s.i., and maximum temperature varies from 160 to 180° C., which is higher than the temperatures used in sulfite pulping. The cooking cycle varies from a little over 1 hour to 5 or 6 hours, depending upon the type of pulp desired. Unbleached softwood sulfate pulps to be used for liner stock are generally cooked in about 1½ to 2¾ hours, and the temperature is brought up rapidly. A typical cooking schedule for container stock involves 1½ to 2 hours to full pressure and ¾ to 1 hour at maximum pressure. For bleachable grades, 4 to 6 hours cooking time is generally used, and the temperature is raised more slowly. In Sweden, cooking conditions are quite different from those practiced in the United States. Cooking times are much longer, a total time of 8 hours and a period of rising temperature of 3 to 4 hours being common. The maximum temperature is about 170° C. Because of the longer penetration period, screenings are relatively low, being about 1½ to 2%, compared with 6 to 10% for American pulps. The active alkali (expressed as Na₂O) is about 14% of the wood weight, and the liquor ratio is generally 4 to 1. By virtue of their special cooking procedures, Swedish sulfate pulps pass through a maximum in strength at a definite cooking time and then decrease in strength rapidly with further cooking. American sulfate pulps do not, as a rule, attain as high a maximum strength, but they reach their maximum strength relatively early in the cooking process and maintain this strength, regardless of length of cooking time.

Alkalies of the concentration used in alkaline pulping dissolve an appreciable amount of wood at room temperature. The rate of dissolution is greatly increased at higher temperatures, the rate being approximately doubled for each 10° C. rise in temperature in the normal pulping range.^{255, 256} Temperature has relatively little effect on the strength properties of the pulp,²⁵⁷ although yield and viscosity of the pulp tend to decrease with increasing temperature. At very high temperatures, the removal of carbohydrates exceeds the removal of lignin; hence, excessively high temperatures should be avoided. Cooks carried out with a slowly rising temperature produce stronger pulp than cooks carried out with a rapidly rising temperature, probably because the concentration of alkali is less when the digester reaches maximum temperature, and hence, there is less attack

²⁵⁵ M. W. Bray and C. E. Curran, *Paper Trade J.* 97, No. 5: 52-57 (Aug. 3, 1933)

²⁵⁶ W. J. Nolan and D. W. McCready, *Paper Trade J.* 102, No. 4: 48-53 (Jan. 23, 1936)

²⁵⁷ J. S. Martin, M. W. Bray and C. E. Curran, *Paper Trade J.* 97, 20: 242-246 (Nov. 16, 1933)

on the cellulose and little removal of hemicelluloses, but considerable removal of lignin. This procedure is generally followed in Scandinavian sulfate mills, whereas American practice is to use a more rapid temperature rise.

For the same concentration of chemical and same chemical application, increasing the time of cooking increases the dissolution of wood. The greatest amount of dissolution occurs early in the cooking cycle. Normally, cooking is complete in the soda process after 1 hour at maximum temperature.²⁵⁸ The effect of total cooking time on pulp yield when spruce is cooked at different temperatures but at constant per cent chemical (20%) and constant concentration (20 g./l.) is shown in Figure IV-15.²⁵⁹ At 140° C.,

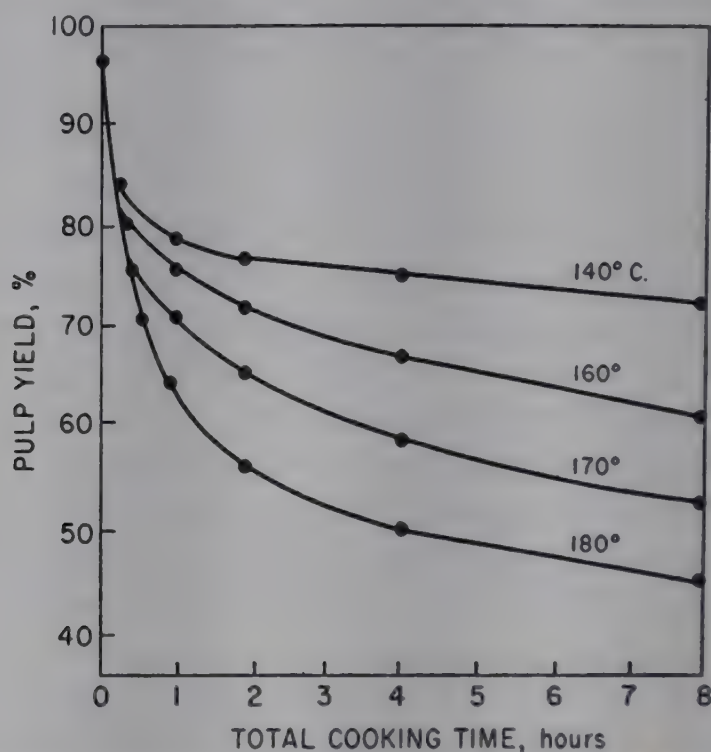


Fig. IV-15. Effect of cooking time on yield of spruce cooked by soda process.

yield falls off at a relatively high value after about 1 hour total cooking, after which there is only a gradual lowering in yield. At 180° C., yield levels off at a much lower value after about 4 hours total cooking time, and there is some further loss in yield with additional cooking time. In the cooking of hardwoods (sweetgum) by the sulfate process, Bray and Martin²⁶⁰ found that the maximum time for complete reduction was 0.5 hour at 170° C. after an initial 1.5 period of rising temperature. Extension of the period at maximum temperature to 3 hours slightly reduced the lignin content of the

²⁵⁸ M. W. Bray and T. M. Andrews, *Paper Trade J.* 76, No. 19: 49-51 (May 10, 1923)

²⁵⁹ M. W. Bray, *Paper Trade J.* 87, 23: 220-226 (Dec. 6, 1928)

²⁶⁰ M. W. Bray and J. S. Martin, *Paper Trade J.* 113, No. 25: 313-324 (Dec. 18, 1941)

pulp, but reduced the yield slightly and did not improve the bleachability or strength of the pulp.

Effect of Sulfidity in Alkaline Pulping

Sulfur compounds have long been known to have a beneficial effect in alkaline pulping. The addition of a small amount of elemental sulfur to soda cooking liquor is known to improve the bleachability, strength, and pulp yield obtained with the softwood species, and to improve the bleachability obtained with the hardwood species.²⁶¹ The amount recommended is from 1 to 2% of the weight of the wood, an amount greater than this being of no beneficial effect. Various mechanisms have been postulated for the reaction of sulfur with sodium hydroxide during the cooking process, but the one probably most widely accepted is that represented by the following formula:



Kress²⁶² believes that a higher proportion of thiosulfate is obtained than indicated by this equation, the exact proportion being affected mostly by the time of reaction and ratio of reactants, and to a lesser extent by the temperature of cooking. Bray and Singer²⁶³ found that the addition of either sodium sulfite or sodium thiosulfate to soda liquor has a beneficial effect on the rate of pulping and on the strength and bleaching qualities of the pulp.

In the sulfate process, sulfur is added in the form of salt cake (sodium sulfate), which is then reduced in the process of recovery to sodium sulfide. Sodium sulfide cannot be used as the sole pulping agent, since it is necessary to have more alkalinity present than can be supplied by a practical recovery operation. There is a minimum amount of sodium hydroxide required for successful pulping, and it is therefore necessary to use additional alkali in the form of sodium hydroxide. When used by itself, sodium sulfide results in a rapid penetration of the wood, uniform cooking, low cooking time, high yield, and high strength, but the pulp is dark colored. The beneficial effects of sodium sulfide are realized in part in the sulfate process.

The sodium sulfide in the cooking liquor hydrolyzes as follows to produce sodium hydrosulfide:



Thus, the sodium sulfide increases the sodium hydroxide content of the liquor and, more importantly, it produces hydrosulfide which exerts a highly beneficial effect on the pulping reactions. The active cooking chemicals in the sulfate process include both the sodium hydroxide and the sodium hydrosulfide. It is customary, however, to express the quantities of the

²⁶¹ M. W. Bray and J. S. Martin, *Paper Trade J.* 113: 35-46 (Dec. 18, 1941)

²⁶² O. Kress, *Paper Trade J.* 119, No. 17: 165-169 (Oct. 26, 1944)

sodium compounds present in the cooking liquor on the basis of the Na_2O content, even though sodium oxide does not exist as such in the liquor. Two terms that are frequently used are the active alkali and the effective alkali, the latter referring to the equivalent sodium hydroxide present. These terms are synonymous for the sodium hydroxide added to the liquor. However, in the case of the sodium sulfide, the active alkali equals its chemical equivalent (2 sodium atoms), whereas the effective alkali equals only one-half its chemical equivalent, since only one NaOH molecule is formed by hydrolysis, although there are two sodium atoms present. Thus, the active and effective alkali for the total chemical present in the liquor may be expressed as follows (all expressed as Na_2O) :

$$\begin{aligned}\text{Active alkali} &= \text{NaOH} + \text{Na}_2\text{S} \\ \text{Effective alkali} &= \text{NaOH} + \frac{1}{2} \text{Na}_2\text{S}\end{aligned}$$

The effective alkali equals the active alkali minus the sodium hydrosulfide.

The percentage of sodium sulfide in the cooking liquor, based on the total titratable alkali, is known as the sulfidity of the liquor. The sulfidity in sulfate cooking liquor depends upon the efficiency of chemical recovery, since this determines the amount of salt cake added as make-up which, in turn, controls the sulfidity. Normally, the efficiency in the sulfate process is about 85% compared with an efficiency of 90% in the better run soda mills,²⁶² but improved efficiency of alkali recovery in sulfate mills has made it increasingly difficult to maintain high sulfidity because less make-up chemical is required and consequently less sulfur is added to the system. The disproportionate loss of sulfur compared with that of sodium in the pulping and liquor recovery processes is another factor making it difficult to obtain a high sulfidity. About 2 to 8% of the sulfur present in the cooking liquor is lost to the atmosphere in the form of gases at the digesters, filters, and evaporators and in a finely divided solid form in the stack gases from the recovery furnace. Using waste liquor for dilution of fresh cooking liquor helps to raise the sulfidity of the cooking liquor. In cases where the addition of salt cake is too low to add sufficient sulfur to the system, the addition of sulfur has been suggested, either at the furnace, to the sludge at the lime burner, to the green liquor, or to the white liquor going to the digester. Other sources of sulfur, in addition to salt cake, which have been used in the sulfate process are sodium sulfite, sodium thiosulfate,²⁶³ "synthetic" salt cake (soda ash and sulfur sintered together), nitre cake, gypsum, and waste effluents from chemical plants (e.g., rayon plants).²⁶⁴

The superiority of the sulfate process over the soda process is due to the presence of sodium sulfide in the cooking liquor. As mentioned above,

²⁶³ M. W. Bray and B. Singer, *Paper Trade J.* 125, No. 8: 81-85 (Aug. 21, 1947)

²⁶⁴ T. T. Collins and P. H. West, *Paper Trade J.* 129, No. 10: 328-332 (Sept. 8, 1949)

substitution of sodium sulfide for part of the sodium hydroxide in the sulfate process greatly increases the rate of delignification and also diminishes the injurious effect of the more active sodium hydroxide on the cellulose and hemicelluloses. Thus, substitution of sodium sulfide for part of the alkali makes it possible to shorten the time of cooking or reduce the maximum cooking temperature, thereby increasing the pulp strength and pulp yield. Figure IV-16, taken from work by Hägglund,²⁶⁵ shows the differences in

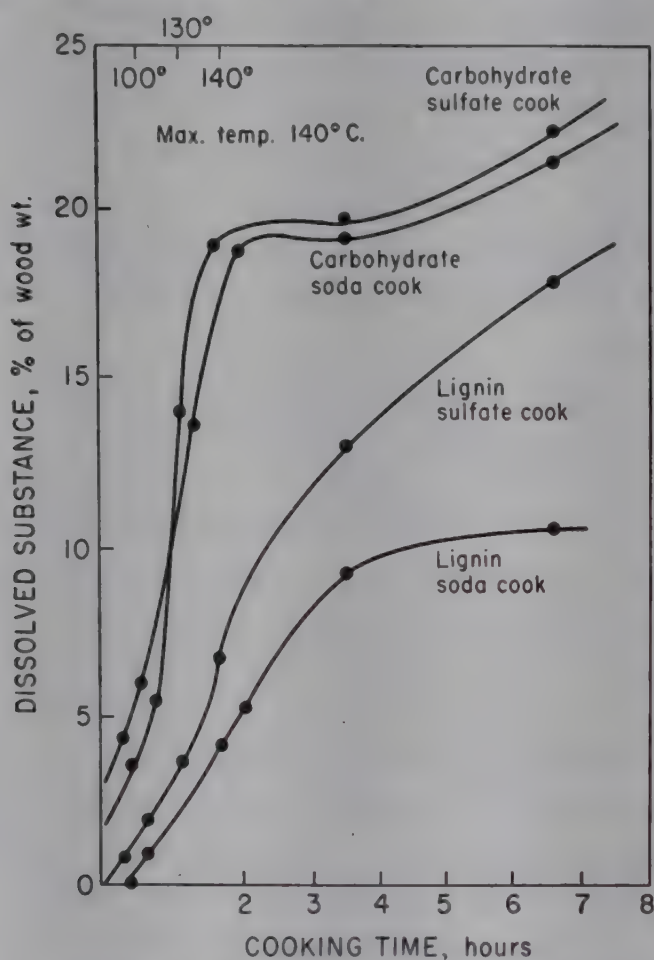


Fig. IV-16. Comparison of soda and sulfate processes for dissolution of carbohydrates and lignin. Maximum temperature 140° C.

dissolution of carbohydrates and lignin during the course of a soda cook and a sulfate cook (30% sulfidity) made on spruce at the same temperature (140° C.) and alkali ratio. The dissolution of carbohydrates is practically the same in the two cooks, but a rapid dissolution of lignin is sustained during the entire sulfate cook, whereas in the soda cook the dissolution of lignin is rapid in the beginning, but eventually decreases considerably. The presence of sodium sulfide in alkaline cooking liquor makes it possible to pulp almost any species of wood. Because of the sodium sulfide in the cooking liquor, sulfate pulping is more rapid, the yield is higher, and the pulp is stronger than obtained in either the sulfite or soda processes.

²⁶⁵ E. Hägglund, *Pulp and Paper* 32, No. 6: 50, 72, 75, 76 (May, 1949)

Even small additions of sulfide to alkaline cooking liquor produce marked changes in the yield and in the physical and chemical properties of the pulp. Any decrease in sulfidity below the optimum value results in a marked loss in strength properties. Soda cooks which are made at zero sulfidity have low strength, low yield, and poor bleachability when coniferous woods are used. The presence of the sodium sulfide in sulfate cooking liquor improves the beating characteristics of the pulp and results in a less brittle pulp than obtained in a normal soda cook.²⁶⁵ The sulfate process tends to produce long, well fibrillated fibers, whereas the soda process tends to produce broken, short fibers (when the same wood species is used).^{265, 266}

Sulfidity varies in commercial sulfate pulping from 20 to 30%, 25% being a good average. In the days when less efficient alkali recovery systems were used, the sulfidity was approximately 33%. Higher sulfidity is required for direct heated digesters than for digesters using indirect heating and forced circulation.

The greatest change in pulp properties is brought about in the range of 0 to 10% sulfidity, but improvements in the pulp are usually noted up to 20 to 30%.²⁶⁷ About 17% sulfidity is required to obtain optimum penetration of pine chips.²⁶⁸ The higher sulfidity generally found necessary in commercial practice acts as a buffer, so that the required amount of alkali needed in the cook can be added without raising the degree of alkalinity to a point detrimental to the cellulose. Under commercial conditions when cooking at normal temperatures, optimum yield is obtained at a sulfidity of about 10%. Strength and bleachability of the pulp generally improve significantly up to about 30% sulfidity when coniferous woods are pulped at normal chemical-to-wood ratio. At very high sulfidities (e.g., 45 to 50%), the pulp produced is very dark and very difficult to beat.

The sulfidity of the cooking liquor can be varied independently of either the active alkali (the total equivalent of the NaOH and Na₂S) or the effective alkali (the NaOH equivalent), but not of both. If the sulfidity is increased and the active alkali held constant, the effective alkali is decreased. If the sulfidity is increased and the effective alkali held constant, the active alkali is increased. In mill practice, it is customary to keep the active alkali constant when changes in sulfidity are made, which means that the effective alkali is decreased. In other words, an equal weight of sodium sulfide is substituted for an equal weight of sodium hydroxide, which means that eventually a point is reached where the percentage of effective alkali (NaOH) is insufficient to dissolve the thiolignins. When this occurs, de-

²⁶⁶ E. Hägglund, *Tappi* 32, No. 6: 241-245 (June, 1949)

²⁶⁷ J. S. Hart and R. K. Strapp, *Pulp Paper Mag. Canada* 49: 151-165 Convention Issue (1948)

²⁶⁸ S. D. Wells, *Pulp Paper Mag. Canada* 46, No. 7: 533-537 (June, 1945)

gnification is inhibited, resulting in an increase in screenings and an increase in bleach requirement. For the chemical-to-wood ratios normally used, increases in sulfidity over about 20 to 30% affect the properties of the pulp as a result of the decrease in effective alkali.²⁶⁷ Sulfidity can be increased to very high values if the effective alkali is kept above a certain minimum.²⁶⁹ In general, the optimum sulfidity for the best pulp properties increases as the total active chemical in the cooking liquor is increased.²⁷⁰

The effect of sulfidity on the properties of pulp obtained from spruce when the total chemical (sodium hydroxide plus sodium sulfide)-to-wood ratio is kept constant at 20% is shown in Table XII, taken from work by

TABLE XII

EFFECT OF SULFIDITY ON YIELD AND PROPERTIES OF PULP FROM SPRUCE
AT CONSTANT ALKALI-TO-WOOD RATIO

Total alkali 20%
Liquor ratio $2\frac{1}{2}$ to 1
Time 3 hours
Temperature 175° C.

Chemicals, lb./100 lb. bone-dry wood		Yield, %			Properties	
NaOH	Na ₂ S	Screened	Rejects	Total	Max. burst	Max. tear
20	—	42.1	3.1	45.2	112	122
13 1/3	6 2/3	42.7	3.3	46.0	165	135
12	8	42.7	5.6	48.3	167	133
8	12	38.2	14.3	52.5	165	124
6 2/3	13 1/3	35.3	21.4	56.7	166	125
—	20	0	—	83.3		

Kress and McGregor.²⁷¹ As can be seen from these results, increasing sulfidity under conditions of low constant chemical-to-wood ratio resulted in an initial increase in yield, but beyond a certain point, resulted in a decrease in acceptable pulp and an increase in screenings. The maximum bursting strength and tearing resistance increased so long as acceptable pulp was produced, but these strength properties became impaired as soon as an inadequate amount of effective chemical was present for pulping. Hart and Strapp²⁷² carried out sulfate cooks on spruce at sulfidities ranging from zero to very high sulfidities under conditions of constant effective alkali

²⁶⁹ M. W. Bray, J. S. Martin and S. L. Schwartz, *Paper Trade J.* 109, No. 17: 224-229 (Oct. 26, 1939)

²⁷⁰ F. S. Hanson, *Paper Trade J.* 112, No. 2: 32-38 (Jan. 9, 1941)

²⁷¹ O. Kress and G. H. McGregor, *Paper Trade J.* 96, No. 24: 302-304 (June 15, 1933)

²⁷² J. S. Hart and R. K. Strapp, *Pulp Paper Mag. Canada* 49, No. 3: 151-165, Convention Issue (1948)

TABLE XIII
EFFECT OF SULFIDITY ON SPRUCE WHEN COOKED AT CONSTANT ACTIVE ALKALI
AND CONSTANT EFFECTIVE ALKALI

Liquor ratio 3½ to 1
Time 3 hours
Maximum temperature 170° C.

Active alkali, % Na ₂ O	Effective alkali, % NaOH	Sulfidity, %		Yield, %		Rejects	Permanganate number	Pulp properties		
		Total	Screened	Screened	Screened			Viscosity	Burst factor	Time to develop max. strength
21.5	27.9	47.2	44.6	44.6	44.6	3.55	35.3	34.0	88	64
21.0	26.4	45.4	43.3	43.3	43.3	2.18	24.5	30.8	93	57
20.9	24.5	44.0	42.4	42.4	42.4	1.60	17.0	37.7	106	54
21.6	22.4	42.3	40.3	40.3	40.3	2.00	18.2	74.9	112	51
21.0	20.2	48.1	45.5	45.5	45.5	2.65	18.0	60.9	113	64
20.8	18.0	47.7	38.8	38.8	38.8	8.90	27.8	97.8	118	64
21.0	26.5	47.7	41.9	41.9	41.9	5.78	28.0	32.5	94	50
22.1	27.0	43.0	41.2	41.2	41.2	1.80	18.9	32.6	90	46
23.5	27.2	44.0	42.5	42.5	42.5	1.80	16.2	34.2	102	47
25.6	26.3	44.1	43.4	43.4	43.4	0.53	13.3	32.8	108	55
31.7	27.4	43.5	41.2	41.2	41.2	2.32	11.3	24.8	100	49
42.4	27.2	42.4	41.5	41.5	41.5	0.88	12.3	31.0	103	51

(21%) and under conditions of constant active alkali (21%). Part of the results taken from their data are shown in Table XIII. An examination of these results shows that when the active alkali was held constant, the bursting strength increased indefinitely with increasing sulfidity up to 65%, but at this point, the permanganate number started to increase and the screened yield started to decrease appreciably. The time for the pulp to develop maximum bursting strength on beating went through a minimum at 20 to 30% sulfidity. When the effective alkali was held constant, bursting strength increased with increasing sulfidity up to about 20%, beyond which the strength leveled off. Increases in sulfidity beyond 20 to 40% when the effective alkali was constant had very little effect.

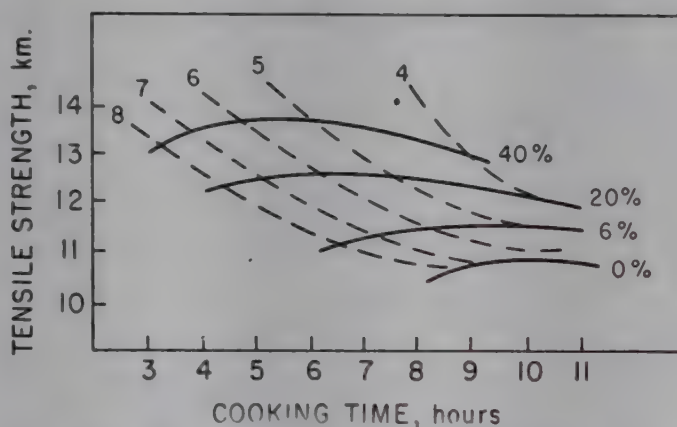


Fig. IV-17. Effect of sulfidity (per cent sodium sulfide) on pulp strength and on cooking time to obtain a definite Roe number (above curves). Per cent sodium sulfide alongside curves at left. Maximum temperature 160° C.

The effect of increasing sulfidity on cooking time (as measured by Roe number) and pulp strength is shown in Figure IV-17, taken from work of Hägglund.^{273, 274} As seen in Figure IV-17, to obtain a Roe number of 5, a cooking time of only 6½ hours is required at 40% sulfidity, compared with a cooking time of 9½ hours at 12% sulfidity when the temperature is maintained constant at 160° C. and the active alkali expressed as sodium hydroxide is maintained constant at 24.2%. Greater tensile strength on beating was obtained from the pulp cooked at the higher sulfidity. Pentosan content, alpha cellulose content, and cuprammonium viscosity of the pulp are not appreciably affected by sulfidity, so long as the effective alkali remains constant.²⁷²

Very little sodium sulfide is consumed during a normal sulfate cook.²⁷⁵⁻²⁷⁷ The bulk of the consumption occurs in the early stages of the

²⁷³ E. Hägglund, *Pulp and Paper* 23, No. 6: 50, 72, 75, 76 (May, 1949)

²⁷⁴ E. Hägglund, *Tappi* 32, No. 6: 241-245 (June, 1949)

²⁷⁵ P. B. Borlew and T. A. Pascoe, *Tech. Assoc. Papers* 30: 570-572 (June, 1947)

²⁷⁶ C. R. Mitchell and F. H. Yorston, Forest Prod. Lab., *Can. Pulp and Paper Lab. Quarterly Rev.* No. 19: 6-16 (July, 1934)

²⁷⁷ P. B. Borlew and T. A. Pascoe, *Paper Trade J.* 122, No. 10: 31-34 (1946)

cook, and there is generally no further consumption of sodium sulfide, once the cook reaches maximum temperature, i.e., about 170° C. At least 50% of the sulfide appears in the final black liquor.²⁷⁸ This is different from the consumption of sodium hydroxide, which is continually consumed during the course of the cook. These effects are shown in Figure IV-18, which shows the approximate consumption of sulfide and hydroxide, as determined by potentiometric titration of the liquor to a pH of slightly over 10 where all the hydroxide and one-half of the sulfide is neutralized.²⁷⁵ The consumption of sodium sulfide is increased as the sulfidity is increased over 20 to 30%, regardless of the change in active or effective alkali.²⁷⁹

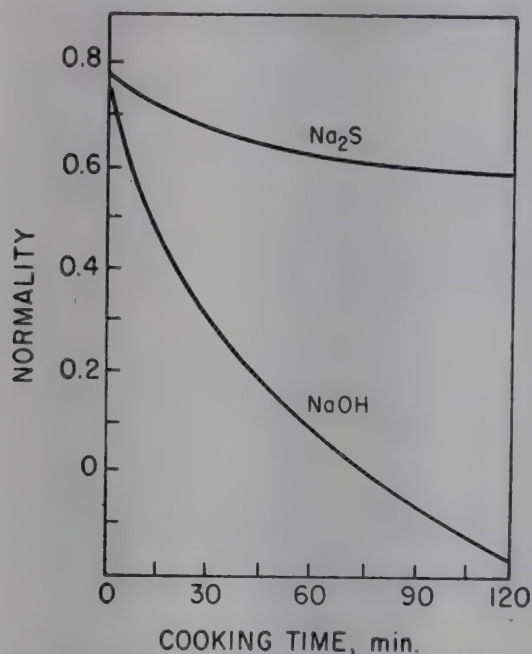


Fig. IV-18. Consumption of sodium sulfide and sodium hydroxide in a sulfate cook.

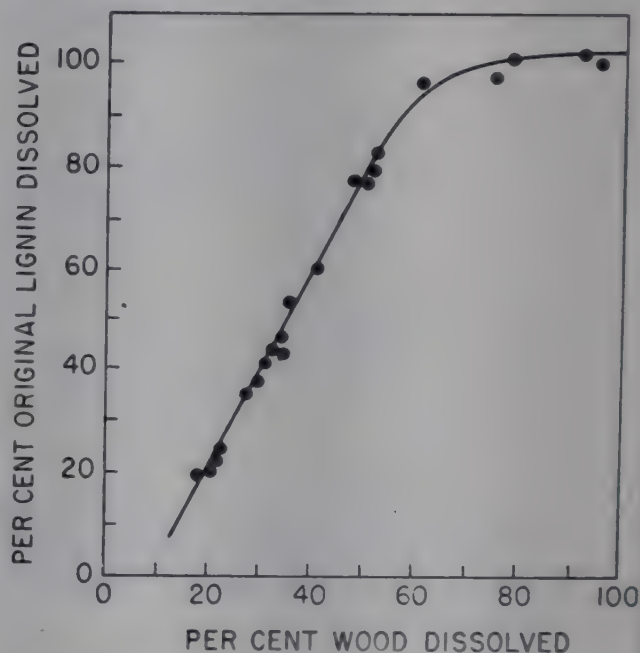


Fig. IV-19. Relation between amount of lignin dissolved and amount of wood dissolved in soda process.

Sodium sulfide is increasingly used up if the concentration of sodium hydroxide falls below a certain minimum.

Reactions in Alkaline Pulping

During an alkaline cook, sodium hydroxide is consumed in reaction with the lignin, carbohydrates, and miscellaneous components of the wood. The consumption of sodium hydroxide is rapid, once the cook reaches maximum temperature, and the consumption continues at a high level during the entire cook until eventually the free sodium hydroxide disappears completely.^{280, 281}

²⁷⁸ O. Kress and J. W. McIntyre, *Paper Trade J.* 100, No. 18: 225-228 (May 2, 1935)

²⁷⁹ J. S. Hart and R. K. Strapp, *Pulp Paper Mag. Canada* 49, No. 3: 151-165, Convention Issue (1948)

Alkali is consumed (1) in reaction with lignin, (2) in dissolution of carbohydrates, (3) in reaction with various organic acids, both those present in the original wood and those produced by hydrolysis, (4) in reaction with resinous matter in the wood, and (5) a small part in adsorption by the fibers. Tannins present in the original wood tend to buffer the alkali in the cooking liquor and gradually release it as delignification proceeds.²⁸² In this way, tannins reduce the effective concentration of alkali during the digestion, resulting in decreased degradation of the fiber and a maintenance of strength properties, although they tend to increase the consumption of chemical. It is generally believed that about one-half of the alkali is consumed by the carbohydrates. Brauns and Grimes²⁸³ found, however, that of the 16% alkali consumed in a normal soda cook, about 1.5% is consumed by neutralization of organic acids, 3 to 4% for solution of the lignin, and most of the remaining 10.5 to 11.5% is used for dissolution of the carbohydrates. In the early stages of the cook, the reaction of alkali with the carbohydrates (mostly the polyuronides) proceeds more rapidly than the reaction with the lignin. The general relation between the amount of lignin dissolved and the amount of wood dissolved is shown in Figure IV-19.²⁸⁴

Alkaline cooking liquors would be expected to have less degrading effect on cellulose than acid (sulfite) cooking liquor. However, cellulose is susceptible to strong alkaline solutions at any temperature and is susceptible to weak alkaline solutions at temperatures higher than 100° C. Coppick²⁸⁵ has shown that in alkaline pulping some depolymerization of the carbohydrates takes place continuously and uniformly during delignification. The degrading effect of alkali is illustrated by the fact that commercial soda pulps generally have an appreciably lower viscosity and D.P. than sulfite pulps. The presence of oxygen is detrimental, and cooking conditions are improved by removing air from the digester and by using reducing agents in the cooking liquor.

Increasing the temperature of cooking to very high levels increases the removal of carbohydrates more than the removal of lignin. At 160° C., the lignin and other encrustants are dissolved about twelve times as rapidly

²⁸⁰ P. B. Borlew and T. A. Pascoe, *Paper Trade J.* 122, No. 10: 31-34 (Mar. 7, 1946)

²⁸¹ P. B. Borlew and T. A. Pascoe, *Paper Trade J.* 123, No. 15: 178-180 (Oct. 10, 1946)

²⁸² J. W. Bard, *Paper Trade J.* 113, No. 12: 137-142 (Sept. 18, 1941)

²⁸³ F. E. Brauns and W. S. Grimes, *Paper Trade J.* 108, No. 11: 136-139 (Mar. 16, 1939)

²⁸⁴ W. J. Nolan and D. W. McCready, *Paper Trade J.* 102, No. 4: 48-54 (Jan. 23, 1936)

²⁸⁵ S. Coppick, *Paper Trade J.* 117, No. 26: 269-271 (Dec. 23, 1943)

as the cellulose,^{286, 287} but at higher temperatures, the ratio decreases, and eventually at very high temperatures the rate of removal of cellulose becomes about equal to that of the removal of lignin and other encrustants. Use of high alkali-to-wood ratios increases the rate of removal of the hemicelluloses and reduces the yield and cuprammonium viscosity of the pulp, although it does improve the bleachability. The effect on the polysaccharides is pronounced when more than 25% sodium hydroxide on the wood weight is used and the concentration of the liquor is increased over 50 g./l. Sutermeister²⁸⁸ believes that 15% sodium hydroxide on the weight of bone-dry wood represents the critical point below which the non-cellulosic constituents are chiefly dissolved and above which cellulose is dissolved, but more than this amount of chemical is used commercially. Meller²⁸⁹ has suggested the use of 40 to 50% sodium hydroxide on the weight of the wood, but this was suggested as a special process for preparing high alpha pulp. It is based upon the preferential removal of the short-chain carbohydrates by the high alkali concentration.

In alkaline pulping, the lignin in the middle lamella is attacked and almost completely removed before the lignin in the outer layer of the secondary wall is attacked.^{290, 291} In other words, alkaline cooking liquor preferentially attacks the intercellular material and leaves intact most of the encrustants between the primary and secondary walls of the fiber,²⁹² which is different from the way in which lignin is removed in the sulfite process. Fairly complete removal of lignin from the primary wall surface was observed in the sulfate process when the lignin content of the fiber was still as high as 8.6%, whereas in the case of sulfite pulps of much lower lignin content, lignin was present in both the primary and secondary walls of the fiber.²⁹³ The relatively high lignin content in the secondary wall of kraft pulps may be the explanation for the difficulty in bleaching these pulps with hypochlorite without greatly reducing the strength of the pulp. Attempts to remove lignin beyond about 4 to 5% in the cooked pulp results in degradation of the fiber and the production of a pulp which is difficult to bleach. Continued cooking at this point results in a loss in yield without appreciably lowering the lignin content of the pulp.

²⁸⁶ S. Arrhenius, *Zellstoff u. Papier* 4: 183 (1924)

²⁸⁷ L. E. Wise, *Wood Chemistry*, p. 719. Reinhold Publishing Corporation, New York, N. Y. (1944)

²⁸⁸ E. Sutermeister, *Orig. Com. 8th Intern. Congr. Applied Chem.* 13: 265-269 (1911)

²⁸⁹ A. Meller, *Paper Trade J.* 123, No. 26: 219-224 (Dec. 26, 1946)

²⁹⁰ L. G. Cottrall, *Paper-Maker* 105, No. 5: TS25-31 (May, 1943)

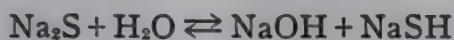
²⁹¹ A. L. M. Bixler, *Paper Trade J.* 107, No. 15: 171-182 (Oct. 13, 1938)

²⁹² T. W. Toovey, *Paper Mill* 62, No. 25: 12-14 (June 24, 1939)

²⁹³ H. F. Lewis, F. E. Brauns and M. A. Buchanan, *Paper Trade J.* 110, No. 5: 58-60 (Feb. 1, 1940)

The exact mechanism by which alkali reacts with the lignin in alkaline pulping is not well understood. It is reasonably certain that sodium reacts with the original phenolic or enolic hydroxyl groups in the lignin molecule to form a sodium salt, and it is also likely that additional hydroxyl groups are produced in the lignin molecule during cooking, and that these in turn react with sodium. Hydrolysis of methoxyl groups in the lignin molecule may be a source of these new hydroxyl groups. This is substantiated by the presence of methanol in the waste liquor and the fact that the methoxyl content of the lignin removed in pulping is less than that of native lignin.

The reactions in the sulfate process are similar to those in the soda process except that there is the additional factor of the sodium sulfide to be considered. This hydrolyzes, as previously shown, according to the following equation, thereby producing sodium hydrosulfide.



The presence of this hydrosulfide acts as a buffer and tends to reduce the degrading effects of the sodium hydroxide on the cellulose. The most important effect of the hydrosulfide, however, is its reaction with the lignin to produce thioglignin. This reaction makes the lignin more readily soluble in alkali and thus reduces the temperature and time required for pulping.²⁹⁴ According to Hägglund,²⁹⁵ sodium sulfide under normal cooking conditions is practically completely hydrolyzed at the beginning of the cook, although Martin²⁹⁶ found that the sodium sulfide is only about 40% hydrolyzed at the beginning of a typical kraft cook and about 90% hydrolyzed at the end. The concentration of sodium hydroxide is the dominant factor in determining the degree of hydrolysis of sodium sulfide.

At the end of a normal sulfate cook, the alkali concentration has become rather low, while the concentration of sodium hydrosulfide is relatively high, which is the reverse of the situation at the beginning of the cook. As mentioned previously, improved results can be obtained by maintaining a more uniform concentration of alkali throughout the cooking period by use of injection cooking. Similar advantage can be obtained by maintaining a more uniform sulfidity throughout the cooking period. This can be done by injection cooking whereby the cook is started with a high-sulfidity white liquor, followed later by an injection of a liquor having a low sulfidity but high sodium hydroxide content.²⁹⁶ Preimpregnation of the wood with black liquor followed by cooking with liquor of relatively low sulfidity accomplishes somewhat the same effect. Preliminary impregnation of pine with black liquor, followed by injection cooking, is said to increase the

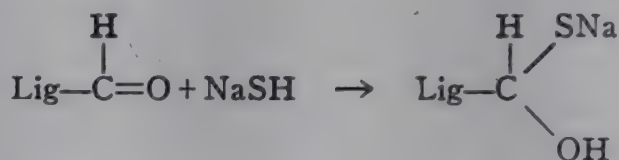
²⁹⁴ S. D. Wells, R. H. Grabow, J. A. Staidl and M. W. Bray, *Paper Trade J.* 76, No. 2: 49-55 (June 14, 1923)

²⁹⁵ E. Hägglund, *Pulp and Paper* 32, No. 6: 50, 72, 75, 76 (May, 1949)

²⁹⁶ G. E. Martin, *Tappi* 33, No. 2: 84-91 (Feb., 1950)

bursting strength by 10% and the tearing strength by 15%, compared with regular sulfate pulp.²⁹⁷

The exact point at which sulfur enters the lignin molecule has baffled chemists for many years. Earlier chemists believed that hydrogen sulfide added to a carbonyl group, thereby forming a relatively unstable mercapto group which was somewhat more acid than a phenolic hydroxyl group and went into solution with alkali more readily. The generally accepted reaction was written as follows:



Recently, Hägglund^{295, 298} found that this reaction does not take place to any extent, as shown by the fact that only a very small amount of lignin goes into solution when the cook is made with plain NaSH. He concludes that no stable mercaptan is formed, but instead that the sulfide replaces hydroxyl groups in the lignin molecule and is mainly bound in the form of an organic sulfide. Delignification takes place in two steps. The first step involves a replacement of hydroxyl groups by alkali-unstable mercaptan groups which are then converted into sulfide groups, the lignin remaining in the solid stage. The second step involves a hydrolytic splitting of the lignin molecule in the presence of the alkali, forming free phenolic hydroxyl groups which make the lignin soluble in alkali. This hydrolytic splitting is made easier by the presence of sulfur in the lignin molecule. Lignin is readily soluble in alkali when the sulfur content of the lignin becomes greater than 5%.²⁹⁵ The sulfur content of commercial sulfate lignin is in the neighborhood of 2.5 to 4.0%, although lignin preparations containing as much as 12 to 18% sulfur can be prepared by special laboratory techniques. According to Hägglund, thiolignin (sulfate process) and alkali lignin (soda process) have, to a large extent, the same molecular and equivalent weights.

Characteristics of Alkaline-Cooked Pulps

Hardwoods are principally used in the soda process. Softwoods are used on occasion, but they constitute a minor source of supply. Most softwoods require drastic cooking conditions to obtain a high white pulp and cannot be cooked in less than 6 to 7 hours, compared with 4 hours for hardwoods, and the yield is lower than that from hardwoods. Softwoods cooked by soda process are weaker and harder to bleach than softwoods cooked by

²⁹⁷ S. D. Wells, G. E. Martin, and D. R. Moltzau, *Paper Trade J.* 119, No. 19: 188-194 (Nov. 9, 1944)

²⁹⁸ E. Hägglund, *Tappi* 32, No. 6: 241-245 (June, 1949)

either the sulfite or sulfate processes. Aspen (poplar) is the most common species used in the soda process, followed by basswood, maple, birch, cottonwood, gum, chestnut, and beech. Birch and poplar make the best pulp, while beech, oak and maple are least satisfactory. Charges of mixed hardwoods are often used.

Wood for the soda process does not have to be as clean as that for the sulfite process, since sodium hydroxide will dissolve bark and decayed areas of the wood. Even knots are not objectionable, inasmuch as they are either dissolved or remain in the form of large pieces which are easily caught on the screens. However, all such extraneous matter reduces the yield, and from the standpoint of economy, it is desirable to have the wood as clean as possible.

Hardwood soda pulp is a pulp of low strength and short fiber length. It is practically always bleached and is commonly used in printing papers, where it produces the desirable properties of high bulk, good formation, high opacity, high degree of softness, good absorbency, and a smooth surface. Soda pulps beat less readily than sulfite pulps, probably because the alkali used in cooking results in a more complete removal of easy-beating, short-chain hemicelluloses and related materials, even though the total pentosan content is high. The lack of easy-beating, short-chain material accounts for the low strength, high absorbency, and high softness of papers containing soda pulp. The bursting strength of papers made with soda pulp is usually between 40 to 55% of that of papers made from spruce sulfite or sulfate pulps.

The sulfate process is the largest and fastest growing pulping process. It is widely used in the southern part of the United States for the cooking of pines, such as longleaf, loblolly, shortleaf, and slash pine. It is used to a small extent in the northern states for the cooking of jack pine and spruce, and to a still lesser extent for hemlock, tamarack, balsam, and white and yellow fir. On the West Coast, the sulfate process is used for cooking Douglas fir, spruce, silver fir, lodgepole pine, cedar, and western hemlock. In the Scandinavian countries, the sulfate process is used for cooking the native softwoods. Hardwoods can be readily cooked by the sulfate process,²⁹⁹ and there is an increasing trend toward the use of hardwoods, both in the United States and in Europe.³⁰⁰ Aspen is the principal hardwood species used in the north; black gum and oak are the principal species used in the south; and birch is the principal species used in Scandinavia. Birch and maple make very good sulfate pulps, but beech sulfate pulp is inferior. In cooking hardwoods by the sulfate process, it is common practice to use a greater charge of alkali per digester and to use a longer period of pressure

²⁹⁹ M. W. Bray, *Paper Trade J.* 120, No. 21: 212-214 (May 24, 1945)

³⁰⁰ E. C. Jahn, *Unasylva* 2, No. 2: 63-66, 88-91 (Mar., Apr., 1948)

raising to balance the higher density of the hardwoods. Hardwood sulfate pulps are more difficult to wash than softwood pulps. The sulfate process has been used in semichemical pulping and for the pulping of certain nonwoody species, such as bamboo.³⁰¹ Mixed furnishes of pine and hardwoods containing up to 25% hardwoods are sometimes used in making low-quality pulps for liner boards. However, the two classes of wood are best cooked separately when making higher grades of sulfate pulp. In making coarse kraft pulps for container boards and cheap wrapping paper, the wood is sometimes used unbarked, but this is poor practice because of the chemical consumed by the bark. The active alkali required per ton of pulp increases at the rate of about 13 lb. for each 1% of bark.³⁰²

Sulfate pulps are produced in higher yield than soda pulps when softwoods are used, although part of the gain in yield attributed to sulfate pulps is due to the fact that much sulfate pulp is cooked "raw" for unbleached, high-strength pulps, whereas most soda pulp is cooked "soft" for bleached grades of book paper. There is less difference in yield between the two processes when hardwoods are used, but the yield is still higher in the sulfate process and the strength of the pulp (burst and tensile) is generally about 50% greater than in the soda process. The yield of kraft pulp obtained from various woods is shown in Table XIV.³⁰³ In both processes, the rate of delignification is greater with hardwoods than with softwoods.

Because of the moderating effects of sodium sulfite, pulping with the sulfate process has less injurious effect on the cellulosic material than does soda liquor. However, in both processes the short-chain, cellulose-like materials are removed to a large extent, while the alkali-resistant pentosans are left in the pulp. As mentioned in the case of soda pulps, these alkali-resistant pentosans remaining in the pulp are not as easily "hydrated" as the shorter-chain material removed during cooking, thus explaining the slower beating qualities of alkaline-cooked pulps compared with those of sulfite pulps. Sulfate pulps look much the same as soda pulps under the microscope (when the same species are used), but sulfate pulps fibrillate readily, whereas soda pulps tend to break down and fracture on beating. Average analyses of a number of typical bleached and unbleached soda and sulfate pulps are shown in Table XV.^{304, 305}

Most sulfate pulps contain long, strong fibers, since the pulp is usually made from long-fibered softwoods. The unbleached grades (kraft) are outstanding for toughness, strength, and durability.

³⁰¹ S. D. Wells, *Southern Pulp & Paper Mfr.* 11, No. 10A: 56-66 (Oct. 31, 1948)

³⁰² G. F. Allo, *Pulp Paper Mag. Canada* 47, No. 3: 116-118 (Feb. 1946)

³⁰³ TAPPI Data Sheets

³⁰⁴ S. I. Aronovsky and E. C. Dryden, *Paper Ind.* 22, No. 3: 253 (1940)

³⁰⁵ L. E. Wise, *Wood Chemistry*, 2nd Ed., pp. 731-752. Reinhold Publishing Corporation, New York, N. Y. (1946)

TABLE XIV
YIELD OF KRAFT PULP FROM VARIOUS WOODS

Species	Yield of moisture-free screened pulp, lb.		Wood required per ton of pulp, cords	
	Per 100 lb. of moisture-free wood	Per cord	Moisture-free pulp	Air-dry pulp
pruce				
White	48	900	2.22	2.00
Black	49	920	2.17	1.96
Sitka	48	900	2.22	2.00
Pine				
Southern	48	1200	1.67	1.50
Northern jack	47	880	2.28	2.05
Western yellow	48	860	2.33	2.09
Fir				
Balsam	48	785	2.55	2.29
Lowland white	48	900	2.22	2.00
Douglas fir	48	1085	1.85	1.66
Hemlock				
Eastern	45	845	2.37	2.13
Western	48	940	2.13	1.92
Hardwoods				
Aspen	56	960	2.08	1.87
Sweetgum	50	1090	1.84	1.65
Southern cottonwood	54	970	2.06	1.86
American elm	50	1145	1.75	1.57
Blackjack oak	45	1410	1.42	1.28

Commercial sulfate pulp has four major types: northern European, southern United States, northern United States, and Pacific Coast. These vary considerably in their properties, because of differences in the species

TABLE XV
ANALYSES OF COMMERCIAL UNBLEACHED AND BLEACHED SODA AND SULFATE PULPS
(BASED ON OVEN-DRY WEIGHT)

	Unbleached		Bleached	
	Soda	Sulfate	Soda	Sulfate
Ash, %	1.1	0.8	0.7	0.7
Ether solubles, %	0.2	0.4	0.5	0.2
Lignin, %	1.6	4.2	0.5	0.1
Fentosans, %	19.7	10.7	18.3	11.3
Cross and Bevan cellulose, %	95.6	93.6	—	—
Alpha cellulose, %	78.7	77.7	71.1	82.8
Alkali soluble (7.14%), %	13.4	10.1	33.0	21.5
Permanganate number	9.5	20.8	2.1	2.4
Copper number	0.7	1.1	3.7	2.4
Viscosity (cuprammonium TAPPI) cps.	27.1	57.1	5.6	14.6

of wood used and differences in the cooking conditions. Northern sulfate pulps are generally made from spruce, although some jack pine is used. Northern spruce sulfate is generally considered superior to the southern grades and often commands a slightly higher price than the southern sulfate made from hard pine, or northern kraft made from jack pine. As a rule, longer cooking cycles are used in making northern sulfate pulps than are commonly used in making southern sulfate. In comparison with northern sulfate, southern pulps contain a higher percentage of thick-walled summerwood fibers, develop more skin substance and fiber debris on beating, and have a lower specific surface area involved in fiber-to-fiber bonding than northern kraft.³⁰⁶ Southern kraft hydrates more rapidly and produces a harder, more "tinny" sheet. It has a higher tearing strength than northern kraft because of its longer, coarser fibers, although some grades contain a small percentage of short hardwood fibers. West Coast sulfate pulp is characterized by very high tear and burst, which is about equal to that of southern sulfate. Scandinavian softwood sulfate pulps are more like the northern United States pulps than the southern grades.

The greatest use for unbleached (kraft) sulfate pulps is in the manufacture of heavy papers for corrugated and solid-fiber board and for fiber drums and fiber cans. Other important uses are for high-strength bag, twisting, gumming, and wrapping papers. Bleached sulfate is stronger than bleached sulfite, and is used in the production of high-grade white papers where strength is important, such as envelope, white bag and wrapping, filing folders, writing papers, printing papers, food containers, charts, tags, waxing, greaseproof, onion skin, and in folding boxboard. Other uses for sulfate pulp in either the bleached, semibleached, or unbleached state include toweling, cable paper, abrasive paper backing, laminated plastics, waxing, cup paper, and many others.

Generally speaking, hardwood sulfate pulps are slightly lower in strength and produce softer, bulkier papers than spruce sulfite pulps,³⁰⁷ but are stronger than corresponding pulps produced by the soda process. Special bleached Swedish sulfate pulps made from birch are, however, higher in strength than bleached softwood and hardwood sulfite, and have about 70 to 80% of the strength of softwood sulfate. Full beating develops maximum strength and produces a hard, rattly paper. These pulps can be used as a filler pulp if charged toward the end of the beating period.

Considerable interest has been shown in the development of high alpha pulp by the sulfate process, particularly from the hardwood species. Ordinary hardwood sulfate pulps are not suited for manufacture into alpha

³⁰⁶ M. W. Bray and J. S. Martin, *Paper Trade J.* 120, No. 3: 25-28 (Jan. 18, 1945)

³⁰⁷ K. D. Running, *Pulp Paper Mag. Canada* 41, No. 2: 181-184 (Feb., 1940)

pulp because of their high content of alkali-resistant pentosans.³⁰⁸ It is not feasible to lower the pentosan content by drastic cooking and bleaching, since this degrades the cellulose too much, although Meller³⁰⁹ was able to prepare sulfate pulps of high alpha cellulose content (91–93%) by cooking with about 44% sodium hydroxide on the weight of the moisture-free wood, using relatively low pressures and temperatures. It is possible to prepare hardwood sulfate pulps containing low percentage of pentosans by first pre-treating the wood with acid solutions or chlorine water to render the normally alkali-resistant pentosans soluble in the alkaline cooking liquor.^{310–313} In Germany during World War II, a rayon-grade pulp was made from beech by first hydrolyzing the wood in dilute sulfuric acid to remove the hemicelluloses (which were removed as sugars), and then cooking by the sulfate process. Special processes used for making high alpha pulps by the sulfate process are discussed further in the chapter on bleaching (alkaline purification of pulps).

Recovery of Chemicals from Alkaline Cooking Liquors

In the alkaline cooking processes, it is common practice to recover the alkali from the spent cooking liquors for reuse. Sodium hydroxide is a relatively expensive chemical, and its loss in the recovery process is of serious concern to pulp mill chemists.

The steps involved in liquor recovery are washing of the pulp to remove chemical, concentration of the resulting liquor by evaporation, burning of the concentrated liquor in special furnaces to convert the soda into sodium carbonate, and causticizing of the carbonate by treatment with lime. During causticizing, the sodium carbonate is converted into sodium hydroxide, and calcium carbonate is formed as a by-product which is then removed by settling. The most efficient operation is one in which the cleanest pulp is produced, the loss of chemical is held to a minimum, and the greatest amount of heat is produced. The various steps involved are shown in the drawing below which illustrates the cyclic nature of the process. Points of addition of fresh materials are indicated by heavy arrows.

Losses of chemical occur in pulp washing, sludge washing, lime re-burning and in the furnace. Of a total loss of 300 lb. of sodium sulfate, about 150 lb. equivalent would be lost at the stack, 100 lb. equivalent in the wash room, and 20 lb. equivalent by absorption by the fibers.³¹⁴ In an ef-

³⁰⁸ A. Miller, *Paper-Maker* 110, No. 5: 1043–1052 (Nov., 1945)

³⁰⁹ A. Meller, *Paper Trade J.* 123, No. 26: 219–224 (Dec. 26, 1946)

³¹⁰ G. A. Richter, U. S. 1,787,953 (Jan. 6, 1931)

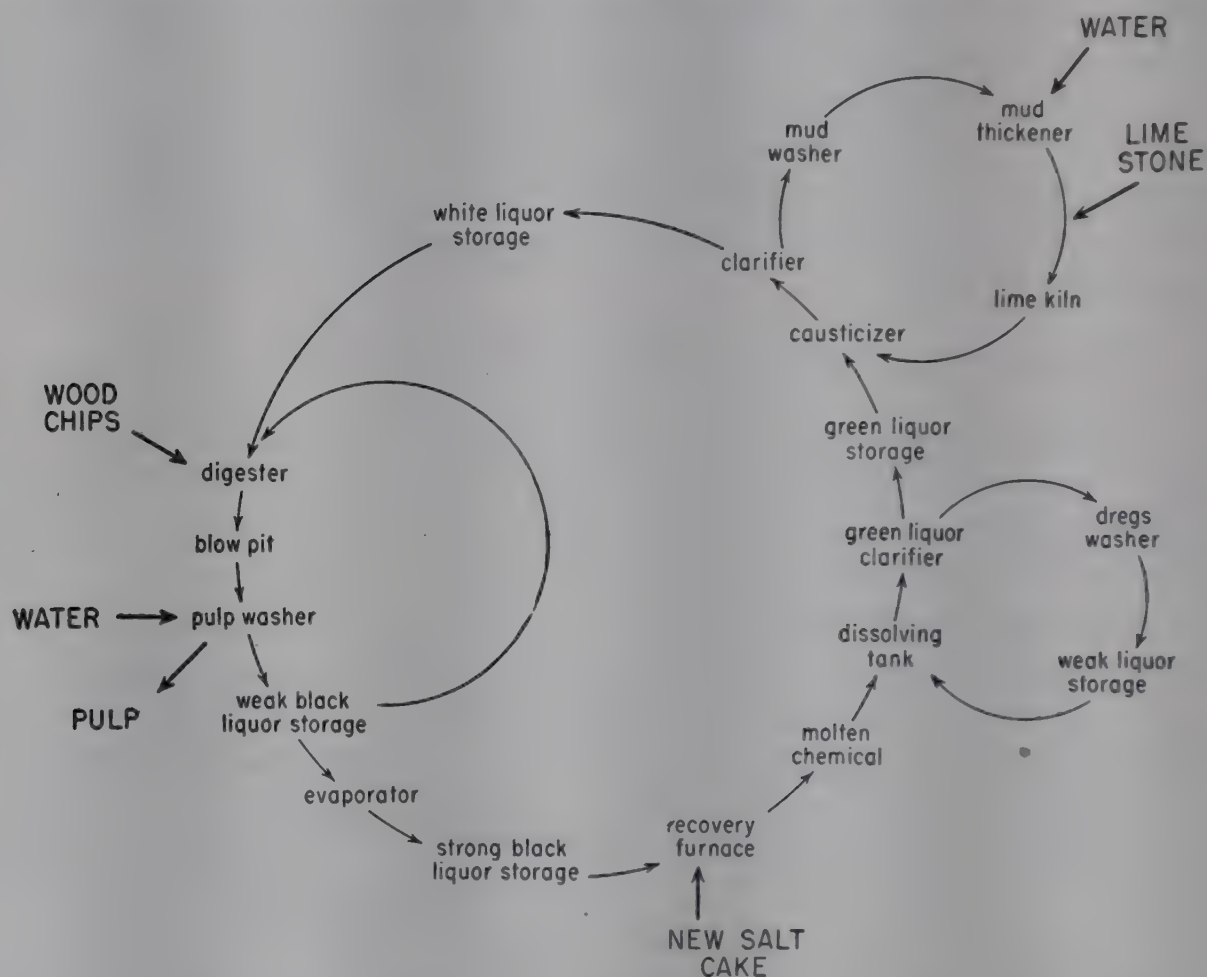
³¹¹ G. A. Richter, U. S. 1,819,002 (Aug. 18, 1931)

³¹² G. A. Richter, U. S. 2,036,606 (Apr. 7, 1936)

³¹³ G. A. Richter, U. S. 1,816,343 (July 28, 1931)

³¹⁴ O. Kress, *Paper Trade J.* 119, No. 17: 165–169 (Oct. 26, 1944)

ficient system, the total loss of chemical should not run over 3 to 5% of the original soda added at the digesters. The losses may be expressed as chemical loss, chemical consumption, or chemical recovery (see standard terms at beginning of section). Total consumption as pounds of sodium carbonate (soda process) or pounds of sodium sulfate (sulfate process) is useful for figuring costs, but does not show the efficiency of operation. For example, a given loss in salt cake per ton may mean a high percentage loss in the case of a mill making raw kraft, whereas the same loss in pounds



per ton would mean a lower percentage loss in the case of a mill making a well-cooked, bleachable sulfate pulp. A percentage figure, e.g., chemical recovery or chemical loss, takes this factor into account.

Washing of Pulp

After cooking is complete, the pulp is blown to a blow pit where it is mixed with black liquor (from the first washing stage) to a consistency of about 3.5%. The stock is then diluted further to a consistency of about 1.0 to 1.3%, screened through coarse (knotter) screens, and pumped to the pulp washers. When making coarse, raw pulps, the pulp may be passed through refiners to break up the fiber bundles before washing. Washing of the pulp serves the dual purpose of purifying the fibers and recovering

the alkali for reuse. The recovery of alkali in this stage should be about 98 to 99% or, in other words, the loss of chemical (amount of chemical left in the pulp) should be less than 30 to 50 lb. of sodium sulfate per short ton of pulp.³¹⁵

Washing should be done with a minimum amount of water. For good operation, the dilution of liquor from the digesters to the evaporators should be less than 1.7 lb. of water per pound of air-dry pulp. Countercurrent washing on multiple-stage vacuum washers or in diffusers (tanks with false bottoms) is used, the first wash being weak liquor from a previous wash, and the final wash being hot water which is run to the sewer. In the newer mills, multiple-stage washers involving three to four stages and, in some cases, five stages, are generally used. About 0.8 to 1.0 gal. of fresh water is used for each pound of pulp in the washing operation.³¹⁵ The wash water temperature is generally about 130 to 150° F. Too high a temperature or too much vacuum on vacuum washers causes excessive foaming.

Washing efficiency is an important factor in recovery, but actually it is impossible to calculate, other than from empirical test data, countercurrent washing efficiency on vacuum filters. It is possible to predict fairly closely the over-all efficiency on so-called multiple-stage washers where all the washing is by repeated dilution and thickening, and all the solids are considered to be soluble and removed in proportion to the liquor removal. Figure IV-20 shows a work sheet which can be used for showing relative efficiencies (based on the above assumptions) for various countercurrent washers. Lientz and coworkers³¹⁶ found that the total soda content in alkaline-cooked pulps after washing is a direct function of the dilution factor, i.e., the quantity of wash water passing through the pulp sheet per unit of pulp washed, but this is not true in all cases. It is important that the production of pulp over the washers be regulated to obtain maximum efficiency. If too much production is called for, extra washing units should be installed, since the soda content of kraft pulp increases almost directly in proportion to the increase in production rate.

The spent cooking liquor from the digesters plus the filtrate from the washing operation is commonly known as black liquor. The black liquor contains practically all the alkali originally added, together with over half the original weight of the wood. In many mills, part of the black liquor is taken from black liquor storage and used for charging the digesters where it acts as a diluent for the fresh liquor. The black liquor not reused in this way is sent to the alkali recovery plant. Sulfate black liquor is tested for specific gravity, amount of organic matter, and concentration of silica, total

³¹⁵ R. C. Richter, *Paper Trade J.* 124, No. 10: 104-105 (Mar. 6, 1947)

³¹⁶ M. Klein, F. S. McCall and J. R. Lientz, *Paper Trade J.* 124, No. 5: 44-51 (Jan. 30, 1947)

sodium, sodium sulfate, total alkali, active alkali, sodium sulfide, iron oxide and alumina, and total sulfur. Samples of black liquor should be analyzed as soon as possible after the sample was taken and the sample should be protected from air. The methods of carrying out the above tests are described in TAPPI Standards. A suitable method for determining sodium hydroxide and sodium sulfide by potentiometric titration has been described earlier in this chapter.

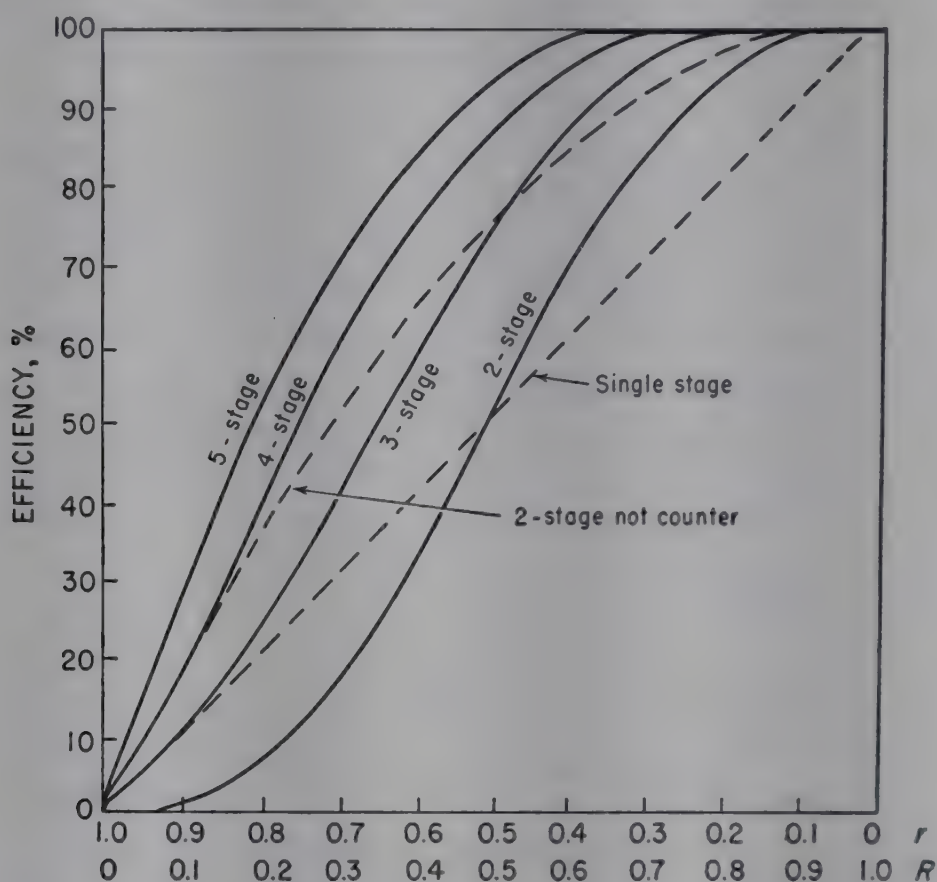


Fig. IV-20. Work sheet for determining relative efficiencies of various countercurrent washers: r =residual stage; R =removal stage.

Evaporation of Black Liquor

The combined black liquor from the washing operation amounts to about 15,000 to 20,000 lb. of liquor per ton of pulp. The solids content of this liquor is generally from 15 to 22%, 17% being a good average. Thus, the total amount of solids in the black liquor varies from about 2,200 lb. for hard pulps to 4,400 lb. for soft pulps.

The dilute black liquor from the washing operations must be concentrated by evaporation so that it can be ignited and burned in recovery furnaces by virtue of the organic matter in the liquor. Evaporation is first done in vacuum, multiple-effect (sextuple) evaporators, usually of the long-tube, vertical-film type, in which the liquor passes upward in the tubes countercurrent to the flow of steam. Thus, the liquor is boiled by steam

obtained from the previous effect, except in the first effect where boiler steam is used. A vacuum of 26–28 in. is applied to the liquor at the weak liquor effect.

The concentration of the black liquor leaving the last effect of the evaporators is about 50 to 55%. The liquor is then concentrated in direct-contact evaporators of the cascade type to a solids content of 55 to 70%, using hot gases at 400 to 600° F. obtained from the recovery furnace. A solids of 55% is about the minimum at which stable combustion can be self-sustained, while 70% solids is the upper limit because of handling difficulties caused by high viscosity.³¹⁷ Too high a solids also limits the capacity of the evaporators and leads to plugging of the evaporator tubes and furnace spray nozzles by salt cake crystallizing out.

Foaming, corrosion, carbonaceous deposits, and scale are some of the problems encountered in evaporation. Foaming is more severe with black liquor from the sulfate process than from the soda process, because more resinous woods are used in the sulfate process. Foaming decreases with an increase in the concentration of the liquor and ceases to become a practical problem at solids over 35 to 40%. Removal of the soap for tall oil recovery reduces foaming troubles. Another remedy sometimes used to control foaming is to add some of the evaporated black liquor back to the fresh liquor entering the first effect. Foaming is far less of a problem in the newer vertical film type evaporators than it was in the older submerged tube evaporators operated with a liquor level in the body of the evaporator.

Recovery Furnace Operation

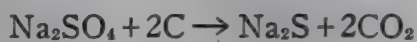
Three things occur in the recovery furnace, in the following order: (1) the remaining water in the heavy liquor is evaporated; (2) the solid matter is decomposed into carbon, inorganic sodium salts, and volatile gases, of which the latter are ignited and burned; (3) the carbon is burned in the presence of hot air. Most of the sodium in the liquor is converted into sodium carbonate because of the excess of carbon dioxide present during burning. Two types of burners are used, rotary and stationary.

In the older soda mills, rotary cylindrical burners are used. In these burners, the carbon is only partially burned away so that the residue is discharged as a black ash containing about 20 to 25% carbon. This carbon represents a loss of potential heat, but in this type of burner, some carbon must be left because the temperature of the ash is intentionally kept low to reduce loss of chemical. Loss of chemical by burning in rotary furnaces is generally about 2 to 50 lb. of soda ash per ton of pulp. In order to make up for the loss of chemical in washing, evaporation, and burning, sodium carbonate must be added at some point after the furnace, the total make-up

³¹⁷ R. K. Allen, *Southern Pulp & Paper Mfr.* 11, No. 5: 46–54 (May 15, 1948)

varying from about 200 to 300 lb. of sodium carbonate per ton of pulp, depending upon the efficiency of recovery.

In sulfate mills and in the more modern soda mills, stationary furnaces are generally used. In the sulfate process, sodium sulfate (and sometimes sulfur) is added as make-up chemical to the concentrated liquor feed (about 150–350 lb. per ton of pulp), and the liquor is then sprayed at a pressure of about 35 p.s.i. on the walls or hearth of the furnace. In one design, rotating and oscillating sprays are used so that the spray reaches all parts of the furnace walls. The liquor is evaporated, and the gases and part of the carbon are burned in the upper part of the furnace, whereupon the dehydrated chemical falls to the lower part of the furnace, and the remaining carbon is burned. Here an essential reaction takes place whereby sodium sulfate added as make-up chemical is reduced to sodium sulfide by the residual carbon. The following endothermic reaction is involved, in which about 3,000 B.t.u. are required per pound of sodium sulfate.



The temperature in the reducing zone is usually maintained at 1700 to 1800° F. An important consideration is the per cent reduction of sulfate to sulfide which normally runs from 88 to 92%, although 94% is possible by close operation.³¹⁸ The reduction should be as high as possible since sodium sulfate has no pulping action.

The theoretical amount of air necessary for the complete combustion of black liquor is about 4¾ lb. of air per pound of black liquor solids. Admission of hot air (300–380° F.) at the primary air ports in the reducing zone of the furnace (about 2.5 ft. above the hearth) should be about 65% of the theoretical in order to maintain a reducing atmosphere (to change as much as possible of the sodium sulfate to sodium sulfide) and to maintain a low fuel bed temperature. The limited supply of air in this zone results in the formation of large quantities of carbon monoxide which, in order to recover the full amount of heat, must be mixed with additional air at secondary air ports higher up in the furnace and burned to carbon dioxide. In order to insure complete combustion of the gases in the secondary zone, excess air over the theoretical must be added at secondary ports (about 15 ft. above the hearth). It is desirable to keep excess air to a minimum to maintain high thermal efficiency, but normally about 10 to 30% air over the theoretical must be used. Temperatures in the combustion zone range from 1800 to 2200° F., but the gases are generally cooled to about 1500° F. before entering the superheater.³¹⁸ The loss of chemical in the waste gases from furnace operation varies from 80 to 150 lb. of sodium sulfate per ton of pulp.

³¹⁸ G. M. Dexter, *Paper Trade J.* 129, No. 21: 445–448 (Nov. 17, 1949)

The recovered chemical is discharged from the bottom of the furnace as a molten stream (smelt) consisting of a mixture of sodium carbonate and sodium sulfide practically free of carbon. This smelt is run into a weak solution of (dissolving) liquor and sent to the recausticizing department. One of the difficult problems in the burning of black liquor is the formation of hard deposits on the evaporator heating surfaces. These chemical deposits come from sublimed chemical and entrained black liquor particles.

The heat generated in burning black liquor is recovered by passing the hot gases (temperature about 1800° F.) into a boiler to generate steam and then through an economizer to recover additional heat. The gas at about 400 to 600° F. is then sent to the direct-contact cascade evaporators. The amount of black liquor solids recovered per ton of pulp generally varies from about 2,700 lb. (kraft pulps) to about 3,500 lb. (bleachable grades), the heat value of which (before salt cake is added) varying from about 6,000 to 7,200 B.t.u. per pound of dry solids, depending on the species used and the degree of cooking. Some of the heat obtained from the black liquor is required for fusing, smelting, and reduction of sulfate, and some of the heat is lost by radiation and sensible heat loss in the stack gases. This theoretically leaves about 80 to 82% of the potential heat for other uses. A net heat recovery (in steam) of 65% of the calorific value of black liquor is often attained in the recovery furnace and boiler, additional heat being recovered as hot water.³¹⁹ This amount of recovered heat is sufficient for all the heat requirements of the pulp mill and leaves some heat for other uses.

Clarification of Green Liquor

The recovered chemical (mostly sodium carbonate) from the recovery furnace is next dissolved in water. In the older soda mills, this involves a leaching of black ash to remove the soluble sodium salts from the insoluble carbon, while in the newer soda and sulfate mills, this involves a dissolving of the hot smelt in weak liquor from the lime mud washer. The resulting liquor is known as green liquor, which derives its name from the color imparted by iron compounds. The impurities in green liquor, i.e., iron compounds, carbon, and refractory material, average about 10 to 15 lb. per ton of pulp. The important chemical tests on sulfate green liquor are for specific gravity and for amount of sodium sulfate, total alkali, active alkali (NaOH and Na₂S), silica, alumina and iron oxide, and reducing agents. It is customary to report the results in grams per liter at 20° C. Methods of making these tests are described in TAPPI Standards.

In the older mills, the green liquor was sent directly to the causticizing

³¹⁹ G. Edling, Trans. Fuel Economy Conference, World Power Conference 12 pp. (1947) through "Progress in Alkaline Pulping," S. D. Wells, *Tappi* 32, No. 6: 35A-41A (June, 1949)

tanks, but in modern mills, the liquor is clarified to remove impurities picked up in the smelting operation. Clarification of green liquor is desirable when producing bleached sulfate pulps and is necessary when the lime (from causticizing) is to be recovered. Clarification is done by treating the liquor with coagulating agents and then settling out the impurities in a tank known as the green liquor clarifier. Among the coagulating agents used are glue and lime. In one process,³²⁰ 5 p.p.m. of magnesium sulfate are added to raw green liquor in a vertical cylindrical draft tube whereby magnesium hydrate floc is formed which absorbs and causes the iron, silica, and suspended solids to settle out of the liquor. The remaining solids can be removed in an anthracite filter. The dregs from the clarifier are diluted with fresh water and are washed on a dregs washer. There are generally about 10 to 15 lb. of dregs per ton of pulp.

Causticizing of Green Liquor

Causticizing consists of reacting lime with clarified green liquor to form sodium hydroxide and calcium carbonate. The threefold purpose of causticizing is: (1) to convert the sodium carbonate into sodium hydroxide, (2) to clarify the resulting white liquor, and (3) to recover and calcine the lime mud. Figure IV-21 shows a process quantity flowsheet for a typical kraft continuous causticizing plant. This flowsheet indicates the major equipment items involved, together with a soda and water balance on the complete system. The flow for the entire sulfate process has been shown in Figure IV-11.

In the causticizing plant, the clarified green liquor is pumped to the slakers, generally after passing through a heat exchanger to adjust to the proper temperature. Lime is added continuously at this point in controlled amounts, depending upon the sodium carbonate content of the green liquor. The milk of lime suspension is then pumped to classifiers for removal of grit and from there to the causticizing tanks. In the causticizing reaction, one molecule of lime reacts with one molecule of sodium carbonate to form two molecules of sodium hydroxide and one molecule of calcium carbonate, as shown in the equation below.



Theoretically, 53 parts of lime are required to react with 100 parts of sodium carbonate, but in actual practice, additional lime must be added to compensate for the impurities in the lime and to provide an excess of about 5% lime for speeding up the reaction. A large excess of lime should be avoided, since excess lime increases the difficulty of washing alkali from the sludge.³²¹

³²⁰ Report on Pilot Plant Experiments, *Paper Ind.* 31, No. 1: 64-66 (Apr., 1949)

³²¹ G. B. Hughey, L. K. Herndon and J. R. Withrow, *Paper Trade J.* 114, No. 9: 105-112 (Feb. 26, 1942)

The causticizing reaction ordinarily goes to about 85 to 90% completion. Increasing the concentration reduces the degree of conversion of sodium carbonate to hydroxide. Increasing the temperature speeds up the reaction in spite of the fact that calcium carbonate is more soluble at higher temperatures. Generally, temperatures in the neighborhood of 210 to 220° F. are used. The presence of sodium sulfide in sulfate green liquor

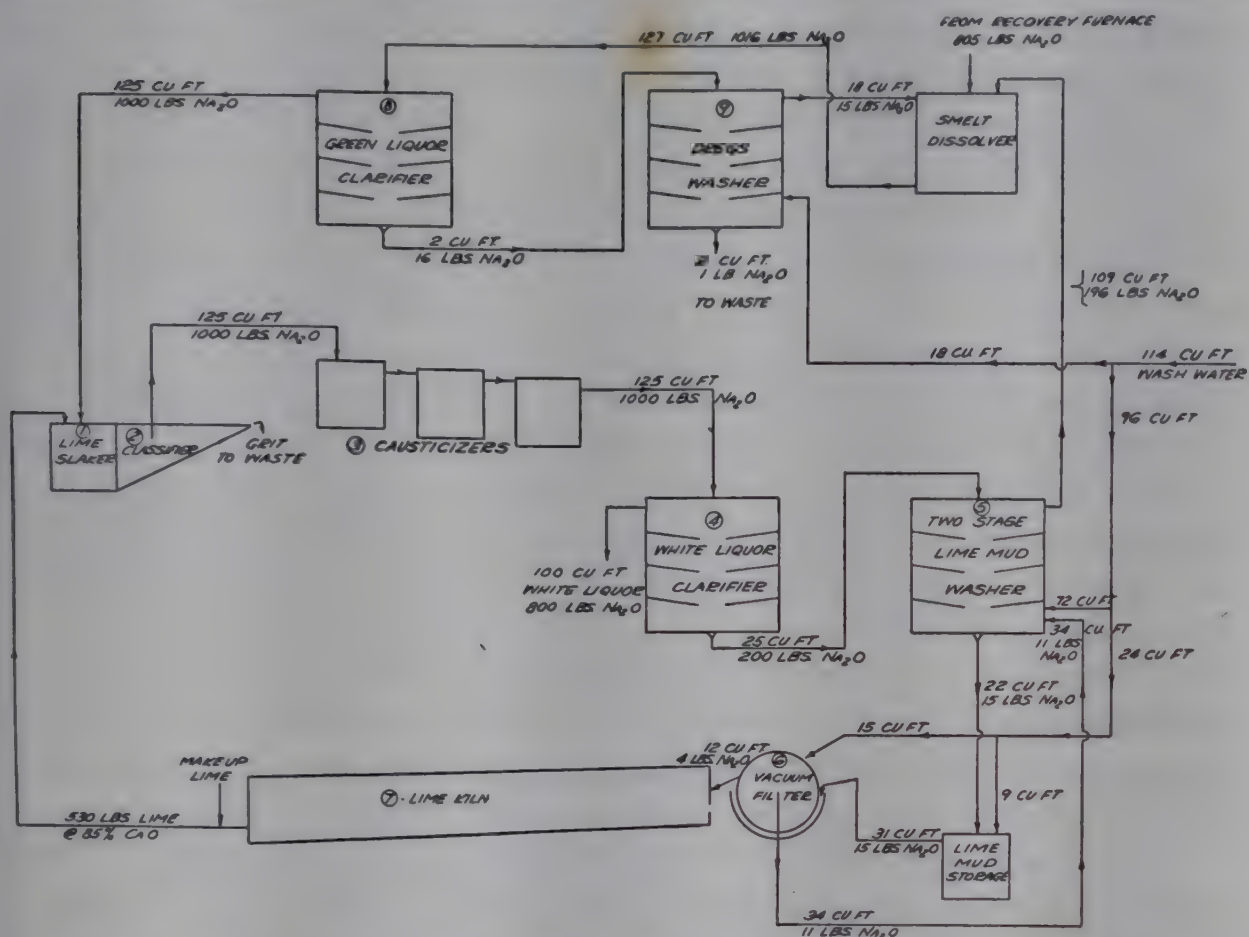


Fig. IV-21. Kraft recausticizing plant—process quantity flowsheet (courtesy The Dorr Company). All quantities are expressed as cubic feet or pounds per ton of air-dry pulp.

Basis: 100 cu. ft. white liquor/ton pulp.

8.0 lb. total alkali as Na_2O /cu. ft.

7.0 lb. active alkali as Na_2O /cu. ft.

30% sulfidity.

White liquor clarifier underflow 33% solids.

Lime mud washer underflow 40% solids.

Filter cake 55% solids.

900 lb. lime mud (dry)/ton pulp handled in steps 1 to 6 inclusive.

15 lb. dregs/ton pulp handled in steps 8 and 9.

Soda reported is total soda as Na_2O .

Volumes reported are liquor volumes without suspended solids.

slows down the rate of causticizing, decreases the equilibrium causticizing efficiency, and lowers the settling rate of the sludge.³²¹ The causticizing efficiency is lowered because the hydroxyl ions produced by the sulfide,

tend to reverse the causticity reaction. The final causticity is further reduced because sulfide increases the titratable alkali, and since causticity is defined as sodium hydroxide over total titratable alkali, any increase in titratable alkali without a corresponding increase in sodium hydroxide will tend to lower causticity.

In continuous causticizing systems, the fully causticized liquor containing calcium carbonate in suspension is pumped into decanters where the lime sludge is removed continuously from the bottom and clean liquor, called white liquor, is removed from the top. The clear white liquor is sent to white liquor storage from which it can be pumped to the digesters as needed. It is important to avoid entrained calcium carbonate in the white liquor, since this decreases the strength of the pulp from the digesters by as much as 10%.³²² Settling of the sludge is improved by high temperature (190 to 200° F.) and thorough, but not too violent, agitation. Sprinkling a small amount of dry starch on the surface of the liquor in the causticizing tank assists in the settling of the sludge. The sludge from the clarifiers is mostly calcium carbonate, but considerable sodium hydroxide is present, and this must be recovered by washing on a lime mud washer. Washing is done countercurrently so that the sludge is mixed in tanks with weaker and weaker liquor, until finally it is washed with fresh water on a vacuum filter. The weak wash water from the lime mud washer is used for dissolving the smelt from the black liquor recovery furnaces. Washing in an efficient two-stage washing process should reduce the soda content of the sludge from about 22% to about 0.5% on a dry lime mud basis.

The lime sludge leaves the vacuum filter at 55 to 60% solids. Most mills dry and reburn the lime sludge to recover the lime for use in causticizing, since the cost of reburning recovered lime is ordinarily only about one-half that of new lime. In some mills, a part of the carbonate sludge is not reburned, but it is refined into a grade of carbonate suitable for the filling of paper. In lime burning, the lime mud filter cake is dropped into a conveyor and delivered to a rotary cylindrical steel kiln lined with refractory where the lime is burned alone or in combination with some fresh limestone. The kiln is sloped about $\frac{1}{4}$ to $\frac{3}{4}$ in. for each foot of length and rotated at about 0.5 to 1 r.p.m. The sludge at constant moisture content is fed into the kiln at one end at a constant rate, while hot air enters at the other end of the kiln at a controlled rate. Water is first evaporated from the sludge, and then as the temperature is increased, the carbonate is broken down into carbon dioxide and calcium oxide. There are three rather distinct zones in the kiln: (1) the feed and drying zone, (2) the central or preheating zone, and (3) the calcining zone. Chains may be utilized in

³²² O. Kress and W. D. Harrison, *Paper Trade J.* 100, No. 2: 272-276 (May 30, 1935)

the drying zone to increase the area of exposure to hot gases by dipping into the lime sludge. Calcium carbonate dissociates at a temperature of 1650° F., but the best operating temperature in the hot zone of the lime kiln is 2300 to 2400° F. Gibbs³²³ calculates that 6,740,000 B.t.u. per ton of lime are required for the burning of lime sludge containing 40% water (4,270,000 B.t.u. for the lime and 2,470,000 B.t.u. for the water). The exit temperature of the gas from the kiln varies from about 300 to 450° F. for kilns equipped with a chain system to as much as 1200° F. in the case of short kilns not equipped with a chain system.³²⁴ The fresh, hot lime is discharged at the end of the kiln in the form of pellets, which can be slaked immediately. In old mills, about 10% of the reburned lime was continuously discarded in order to prevent a build-up of impurities, but this is not necessary in modern systems.

The total loss in continuous causticizing should not exceed 25 to 30 lb. of salt cake per ton of pulp or, in other words, less than 1% of the soda entering the causticizing system. The loss per ton of air-dry pulp should be less than 5 lb. of sodium oxide (of 805 lb. entering the system), and less than 25 to 50 lb. of lime (of 530 lb. entering the system); in some cases, the loss of lime is as low as 10 to 15 lb. per ton of pulp.

Terms Used in Chemical Recovery

Certain standard terms are used for expressing chemical loss and chemical recovery in the alkali pulping processes. These are listed below for both the soda and sulfate processes. In the soda process, the new chemical is sodium carbonate (expressed as Na_2O), whereas the new chemical in the sulfate process is sodium sulfate (expressed as Na_2O).

Chemical recovery is a percentage obtained by dividing the total alkali to the digesters minus the new chemical, by the total alkali to the digesters after correcting for any change in liquor inventory.

Total chemical loss is a percentage obtained by dividing the new chemical by the total alkali to the digesters.

Chemical loss in pulp washing is a percentage obtained by dividing the total alkali to the digesters minus the total alkali to the evaporators, by the total alkali to the digesters.

Chemical loss in evaporators and furnace (sulfate process) is a percentage obtained by dividing the total alkali to the evaporators plus the new chemical minus the total alkali in the green liquor, by the total alkali to the digesters.

Chemical loss in evaporators and furnace (soda process) is a percentage obtained by dividing the total alkali to the evaporators minus the total alkali in the green liquor by the total alkali to the digesters.

Chemical loss in recausticizing and mud washing (sulfate process) is a percentage obtained by dividing the total alkali in the green liquor minus the total alkali in the white liquor by the total alkali to the digesters.

³²³ R. Gibbs, *Paper Ind.* 31, No. 9: 1070-1073 (Dec., 1949)

³²⁴ W. H. Tock, *Paper Mill News* 73, No. 9: 12, 14, 16 (Mar. 4, 1950)

Chemical loss in recausticizing and mud washing (soda process) is a percentage obtained by dividing the total alkali in the green liquor plus the new chemical minus the total alkali in the white liquor, by the total alkali to the digesters.

Chemical consumption is expressed as number of pounds of new chemical (either Na_2CO_3 or Na_2SO_4) per ton of air-dry pulp produced per day.

Recovery of Lignin from Alkaline Liquors

Lignin, as lignin, can be recovered from waste alkaline cooking liquor more readily than from waste sulfite liquor. Mild acid treatment of black liquor releases about 50% of the sodium lignates which can then be separated and converted into lignin by stronger acid treatment. In one process, the black liquor is carbonated with flue gas to reduce the pH and precipitate the lignin in the form of lignin acid salts. The gas may be bubbled through the liquor, or the liquor may be sprayed into a rising column of the gas. About 40 to 60% of the lignin is precipitated which, upon heating to 90° C., melts in the form of a viscous tar. This tar is separated from the rest of the liquor by decantation, dissolved in hot water, and the lignin is precipitated, using sulfuric acid under controlled conditions. The precipitate is then filtered and washed. Recent engineering improvements have been made in the stepwise purification of alkali lignin.³²⁵

Purified lignin from alkaline cooking liquors has been suggested for many uses. Both hardwood lignin and softwood lignin have been produced. One of the uses is as a filler in plastics and resin-impregnated papers. Alkali lignin which has been condensed with long-chain or aromatic amines, aldehydes, or other materials, has been suggested for use in asphalt (as a binder for the stone) and for use in plastics, but the cost is high. Alkali lignin has been used as a reinforcing agent in rubber,³²⁶ for which purpose it is best given an oxidative treatment.³²⁷ It has been used in lead-acid storage batteries as an absorber.

Derivatives of alkali lignin offer promise as flavorings, medicinals, and preservatives. Some of the commercial alkali lignins obtained from hardwoods by the soda process are Meadol (Mead Corporation) and Tomlinite and Arborite (Howard Smith). A commercial coniferous lignin obtained by the sulfate process is sold under the name "Indulin" (West Virginia Pulp and Paper Company).

Recovery of Tall Oil

Pines contain a relatively high percentage of oil, both of the resinous type and the fatty acid type. This is recovered in the sulfate process as crude tall oil, a material containing mainly fats and resins.

³²⁵ G. H. Tomlinson and G. H. Tomlinson, Jr., Canadian Patent 448,476 (May 11, 1948)

³²⁶ J. J. Keilen and A. Pollak, *Ind. Eng. Chem.* 39, No. 4: 480-483 (Apr., 1942)

³²⁷ R. A. V. Raff, *Paper Trade J.* 128, No. 1: 54 (Jan. 6, 1949)

Tall oil, in the form of its sodium salt, is present in the relief liquors which are drawn from the digester at intervals and stored in the black liquor storage tanks. This material is lighter than water and tends to rise to the surface of the tank where it can be readily skimmed off. The amount of these skimmings varies from 100 to 300 lb. per ton of pulp, depending upon the species of wood, season of year, time of aging of stored wood, and other similar conditions. In some mills, the tall oil is taken off the liquor at some point in the evaporators, usually when the black liquor contains about 25 to 28% solids.

After the surface layer is separated from the body of the black liquor, it is acidified to produce a dark liquor which, because of its oily nature, is known as tall oil. The various steps in the recovery of tall oil from skimmings are as follows: (1) the preparation of a sulfuric acid solution, (2) the addition of the washed soap stock to the sulfuric acid solution until the normality is reduced to about 0.3 N, (3) boiling the mixture for approximately 1 hour, (4) setting the mixture for about 4 to 5 hours, (5) skimming or floating off the top layer of crude tall oil.

The yield of crude tall oil obtained from pine in American mills varies from 50 to 90 lb. per ton of pulp. In Scandinavian mills, up to 70 to 90 kg. of tall oil are obtained per ton, which is, respectively, a yield of 50 and 70% of the theoretical.³²⁸ Spruce yields only about 20 to 25% as much tall oil as pine. An important factor affecting the yield of tall oil is the duration of storage of the wood before pulping, since aging promotes oxidation of the fats and resins to compounds which do not separate from the digestion liquor.

Tall oil varies greatly in composition from mill to mill, but always contains resin acids (mostly abietic) and fatty acids. Tall oil from southern kraft mills generally contains from 40 to 60% resin acids and about 30 to 60% fatty acids, together with about 5 to 10% unsaponifiable matter, and 1% of ash and moisture. Canadian tall oils have been reported as having from 44 to 54% fatty acids and 12 to 36% resin acids.³²⁹ Juvonen³²⁸ reports Finnish crude tall oils as having 51 to 59% resin acids, 29 to 36% fatty acids, and 9 to 11% unsaponifiable matter. In the fatty acid component, there is a high percentage of linoleic acid (50–80%), oleic acid (18–45%) and linolenic acid (5–15%), and a smaller percentage (5 to 11%) of saturated fatty acids such as stearic and palmitic. About 3 to 5% sterols are present in crude tall oil; some tall oils are rich in phytosterols, which has aroused interest in the use of tall oil as a cheap source of

³²⁸ V. V. Juvonen, *Paper Trade J.* 130, No. 1: 27–29 (Jan. 5, 1950)

³²⁹ G. N. B. Burch, A. C. Shaw and R. V. V. Nicholls, *Pulp Paper Mag. Canada* 48, No. 3: 127–132, Convention Issue (1947)

vitamin D and certain hormones. The resin acids in tall oil are principally abietic acid, pyroabietic acid, and dextropimaric acid.

Tall oil can be distilled to yield a refined tall oil which is generally used in making soap. A distilled resin product can be crystallized out of the distilled oil and used as a sizing agent for paper and as a resin in lacquers.³²⁸ Tall oil has been sulfonated and used as a substitute for sulfonated castor oil.

Recovery of Sulfate Turpentine

The vapors from the relief of sulfate digesters contain steam, turpentine, and inert gases. The steam may be recovered either by condensing in an accumulator (as done in sulfite mills) or by use in the heating of wash water.

The recovery of crude turpentine, or pinene, as a by-product from the relief of sulfate digesters has increased greatly in recent years, and production now almost approaches that of gum turpentine.³³⁰ Recovery is commercially feasible when pines of high resin content are used. The recovery

TABLE XVI

YIELD OF TURPENTINE FROM VARIOUS SPECIES OF SOUTHERN PINE

Wood used	Gallons turpentine per ton air-dry pulp
Slash and longleaf pine	2.8-4.3
Loblolly, shortleaf, and Virginia pine	1.5-2.7
Jack and white pine	1.5-3.1

process consists of passing the relief gases first through a separator to remove entrained liquor and fiber, and then through a condenser to condense the turpentine. The relief gases enter the separator tangentially and whirl in an annular space formed between the shell and the riser. The heavy liquor and pulp particles are thrown to the sides, due to centrifugal force, and drain to the bottom outlet. The air-vapor mixture rises into the condenser where it is cooled by countercurrent flow of cold water to a temperature of 125° F. Considerable water condenses with the turpentine, and this is removed at the bottom of a special decanter while the turpentine is drained from the surface.

The yield of turpentine varies somewhat, depending upon the species of pine, season of year, ratio of heartwood to sapwood, and the age of the wood. Approximate yields to be expected are given in Table XVI for a number of southern pines.³³¹ In general, the best turpentine and greatest yield is obtained when the digester is relieved at low temperatures.³³²

³³⁰ P. O. Powers, *Paper Trade J.* 126, No. 5: 39-42 (Jan. 29, 1948)

³³¹ W. P. Lawrence, *Paper Trade J.* 124, No. 21: 230-232 (May 22, 1947)

³³² *Southern Pulp and Paper Mfr.* 11, No. 2: 52-56 (Feb. 15, 1948)

The composition of sulfate turpentine is about 50 to 60% alpha-pinene, 15 to 20% beta-pinene, and 10 to 15% monocyclic terpenes. Sulfate turpentine is used in the varnish industry and for the manufacture of plastics, camphor, and other chemical products. It has, however, a decided odor due to the presence of a small amount of mercaptans, and must be purified by fractional steam distillation to compete with gum turpentine. Some pine oil is recovered in the process.

Recovery of Other Materials

The gases and black liquor from alkaline pulping contain many other chemicals, in addition to those already mentioned, but in general, these chemicals are not worthy of recovery. Methanol has been recovered by distillation of the condensed relief gases and evaporator condensate, but the product obtained cannot compete with methanol from other sources.

Waste gases from sulfate pulping contain highly odorous substances (hydrogen sulfide, mercaptan, and methyl sulfide) which are a public nuisance in built-up areas. Most mills do not practice any extensive form of odor control at the present time. However, it is possible to remove the odor and effluent nuisances associated with sulfate pulp mill operation by passing the waste gases and black liquor through an oxidation tower where the sulfur compounds are oxidized so that they are removed from the liquor and gas effluents and retained in the cooking cycle.^{332a, b} Another method of odor elimination is to burn the gases from digester relief and from the blow tanks in a regular furnace and then to oxidize the combusted gases using effluents of the bleaching plant or to dispose of the gases by means of a stack of considerable height.^{332c}

MECHANICAL PULPING

In chemical pulping, chemicals are used for dissolving and removing the lignin which holds the fibers together, thus causing the wood to disintegrate into its component fibers. It is possible also to use purely mechanical methods for disintegrating wood into a fibrous state without the use of chemicals. By far the most important of the mechanical processes is the process used for making groundwood. This process, which was developed about 1844, involves the wet grinding of wood into a fibrous mass by means of a large revolving grindstone. Logs of wood are held with pressure against the surface of the stone, and as the stone grinds the wood into fibers, a stream of water is sprayed on the stone to carry the pulp away. The

^{332a} G. H. Tomlinson, G. H. Tomlinson II, J. N. Swartz, H. D. Arloff and J. H. Robertson, *Pulp Paper Mag. Canada* 47, No. 9: 71-77 (Aug., 1946)

^{332b} W. O. Hisey, *Tappi* 34, No. 1: 1-6 (Jan., 1951)

^{332c} P. Ghisoni, G. Bozza and P. Colombo, paper presented at the 36th Annual Meeting of TAPPI, New York City, Feb. 19-22, 1951

logs are held against the stone in transverse fashion with the length of the log parallel to the axis of the grindstone, because the longest fibers are obtained in this way.

Groundwood pulp differs from chemical pulp in that it contains practically all the lignin of the original wood, and the fibers do not exist as individual entities, but rather as fiber bundles and fragments of fibers. The yield is about 90 to 95% of the original wood, compared with about 50% for chemical pulp. One cord of spruce yields about one ton of groundwood.

About 2 to 6 gal. per minute of water (at 15–50 p.s.i.) are sprayed on the stone on the down running side for each ton of pulp produced. This forms a slush of stock which is collected in a pit under the stone. The bottom part of the grindstone is immersed in this stock in the grinder pit to a height determined by the height of dam boards. Immersion of the stone in this way aids in cleaning the stone, lubricates the surface, and acts to equalize the temperature of the stone.

Excess pulp from the grinder pit flows over the dam into the stock line and is screened through a coarse screen, called a bull screen, to remove the coarse splinters and unground wood. Next, the stock is passed through a knotter screen ($\frac{1}{4}$ - to $\frac{1}{8}$ -in. holes) where the smaller splinters and fragments are removed, then through primary screens equipped with holes about 0.050 in. in diameter, and finally through fine screens and settling devices to remove the foreign matter which is heavier than the fiber. The "tailings" or rejects from the screening operations are used in making a coarse mill wrapper or given further refining to reduce them to acceptable size. The accepted stock is thickened and stored in slush form or put up in the form of wet laps (67% moisture).

Recently, the selective refining of groundwood pulps has been proposed. In this process, the grinding would be adjusted to obtain 25 to 40% rejects, instead of the 3 to 5% rejects normally obtained. These rejects would then be selectively refined and screened into coarse fractions suitable for boards, medium fractions suitable for book papers, and fine fractions suitable for tissue. So far, this practice has not been followed to any extent, although it does have some merit from the standpoint of lower power consumption and greater utility of the wood.

A flow chart of a typical mechanical pulp mill is shown in Figure IV-22.

Types of Grinders

Grinders are of two principal types, continuous and intermittent. Intermittent grinders, which were the earlier development, first employed a lever or screw arrangement for producing the necessary thrust of wood against the stone and, in modern designs, employ a hydraulically operated

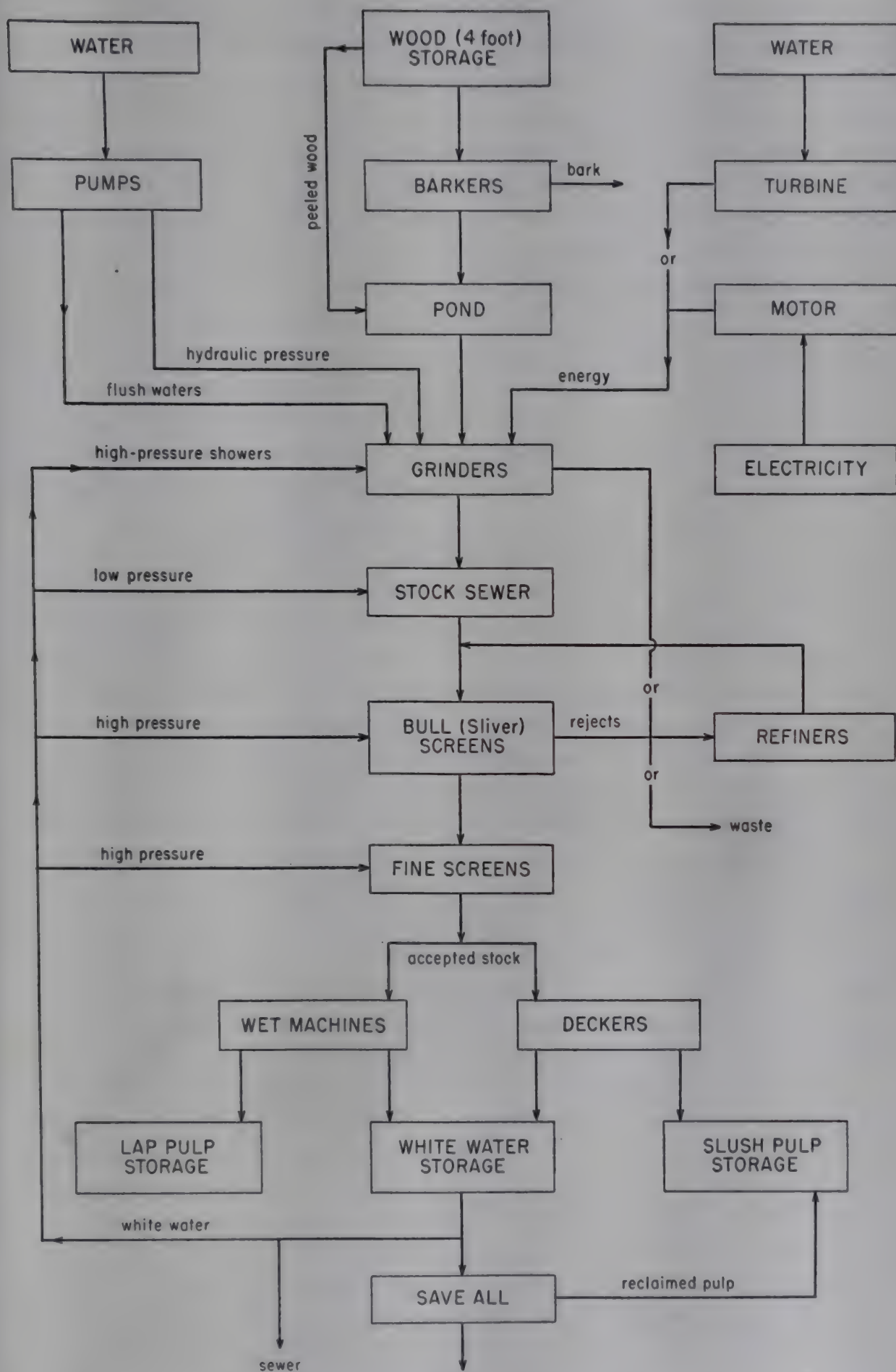


Fig. IV-22. Flow chart of mechanical pulp process.

pressure foot. There are two principal forms of intermittent grinders, the pocket type and the magazine type. Pocket grinders may have two, three, or four pockets located about the top part of the grinder. The wood is loaded manually into pockets from the side when the pressure foot is withdrawn for a new charge. The wood used in pocket grinders is rather short, usually 24, 32, or sometimes 48 in. in length. The production of pocket grinders is relatively low compared with other grinders, and generally varies from 3 to 20 tons of air-dry pulp per stone per 24 hours.

The hydraulically operated magazine grinder was first developed by Voith in 1910. This grinder had two pockets almost directly opposite each other with a magazine located between where the logs were stored. When the hydraulically operated pressure foot of the magazine grinder is withdrawn for a new charge, the wood automatically falls from the magazine into the pocket. When the space is filled with wood, the ram reverses and presses the wood against the stone, the whole operation taking less than 30 seconds. In order to maintain a relatively steady load, magazine grinders are installed in pairs with a synchronous motor of about 4,000 to 5,500 hp. equipped with a timing device which permits only one pocket to be filled at a time. Magazine grinders use larger stones, have more grinding area, and operate at higher peripheral speeds than pocket grinders, which results in increased production of pulp per stone. Handling of the wood is easier than in pocket grinders, since the magazines are filled from the floor above the grinder. The speed of the stone is about 240 to 250 r.p.m. and the production varies from about 20 to 40 tons of air-dry pulp per stone per 24 hours. The Waterous is an example of a magazine grinder.

A variation of the magazine grinder, related to the Waterous, is the Great Northern grinder. This is a two-pocket grinder which has low magazines located above each pocket. The logs are fed to the magazines from an overhead conveyor, and from there are dropped into the pocket when the pressure foot is withdrawn for filling. The magazines hold enough wood for a single charge of the pocket, which facilitates loading of the pocket with the correct amount of wood.

Continuous grinders differ from intermittent grinders in that the wood is fed to the stone without interruption. Continuous grinders were developed at a later date than the intermittent grinder, the primary object in their development being to increase production. The principal continuous grinders are the pocket type (e.g., Kamyr), the chain type (e.g., Warren and Voith), and the rotary type (e.g., Roberts). The Kamyr is a two-pocket, hydraulically operated, continuous grinder which is equipped with a spring device for holding the wood under pressure while the pressure foot is withdrawn to receive a new charge so that the advance of wood is practically continuous. This grinder is used principally in Europe.

In the Warren and Voith grinders, the wood is placed in a central magazine over the stone and from there it is pulled downward continuously to the stone by means of specially designed chains running in grooves down the sides of the magazine. Dogs on the chains grip the sides of the outer logs and impart a downward thrust to the logs held in the magazine.

The Roberts is a more modern continuous grinder of the rotary type in which the stone is set eccentrically in an inside-serrated cast iron ring which forms a crescent-shaped pocket at about the seven o'clock position. The ring revolves slowly (about one revolution in 3 to 5 minutes) in the same direction as the stone, thus forcing the wood under pressure in a gradually constricting pocket. Stone speed in the Roberts grinder is about 3,500 or more feet per minute, and the unit pressure is about 33 p.s.i.³³³ The pulp is discharged from both ends of the stone, dams being used to regulate the depth of stock held in the grinder. The load is held constant by regulating the flow of oil to the fluid motor.

Variables in Mechanical Pulping

The principal variables in mechanical pulping are stone surface, stone speed, grinding pressure, power input, energy consumption, production, temperature of grinding, consistency of grinding, freeness and strength of pulp, and wood variables. These variables are discussed separately in the following sections, but it should be pointed out that they are interrelated one to another, and consequently cannot be completely isolated for individual study. There is a definite relationship between pulp properties, such as freeness and strength, and grinding characteristics, such as energy consumption and production.

Large amounts of energy are required to convert wood into groundwood, and hence energy consumption is the most important factor in mill operation. Grinding characteristics are defined by the energy consumption per ton of pulp and by the tonnage produced if the quality of the pulp, stone surface, pressure, and pit temperature are held constant. The principal operating variables are stone surface and grinding pressure. In order to maintain production and energy consumption at acceptable levels, it is necessary to resharpen the stone at regular intervals during grinding to reduce the pressure.

Stone Surface

Grindstones used in mechanical pulping are composed of hard grit embedded in a softer matrix. Stone surface is one of the principal factors in determining the quality of groundwood, grit sharpness, pattern, smoothness, and uniformity being the most important considerations. One of the con-

³³³ R. S. Magruder, *Tappi* 32, No. 1: 29-35 (Jan., 1949)

ditions necessary for the production of good pulp is projection of grit above the surface of the matrix in the stone surface.³³⁴ The grit must be of the proper type for the grade of pulp being produced; stones with coarse grit tend to produce coarse, shivy pulp, whereas stones with fine grit tend to produce fine pulp. The corners of the exposed grit should be rounded off to minimize cutting of the fibers. Increased grit coarseness increases the strength at constant freeness, but tends to reduce the production.

Both natural sandstones and artificial pulpstones are used, the latter being far more important. In natural sandstones, the grit consists of small particles of quartz. Artificial stones are made by mixing grit of the proper sizes (either silicon carbide or aluminum oxide) with a vitrified bonding agent (consisting of clay, feldspar, flint, and other materials) in proper amount to obtain the desired texture and hardness of stone. The stones are made in wedge-shaped segments which are jointed together in the final pulpstone. Artificial stones are more uniform, have longer over-all life, are available in larger size, and require less frequent dressing than natural stones. They are good for between 10,000 to 60,000 cords of wood, depending on the hardness of the stone and species of wood, compared with an equivalent life of about 1,200 cords for natural stone. The pulp produced from artificial stones is generally longer fibered and has a higher freeness than the pulp produced from natural stones.

Before being used, pulpstones must be dressed, that is, the surface of the stone must be treated lightly with a burr which rotates in contact with the stone and roughens its surface. This produces a definite cutting pattern by exposing the grit and provides grooves in the stone surface where the fibers remain protected until they are washed free by the shower water. Burring can be done by hand or with mechanically or hydraulically operated stone-sharpening lathes. There are four principal patterns of burrs, the straight cut, spiral, thread, and diamond shape. The thread burr cuts grooves in the stone perpendicular to the axis of the stone; the straight burr cut grooves parallel to the axis of the stone; the spiral burr cuts grooves at an angle to the axis of the stone; the diamond burr (a combination of thread and straight burr) cuts little pyramids in the stone. The stock produced with a diamond burr is generally short and stubby, but the production is high because of the large number of exposed grits. The straight burr produces long, shivy stock. The thread burr tends to produce a short-fibered stock due to regrinding of the stock on the stone face; it is used mostly for light dressing of the stone surface. The most popular patterns are obtained with spiral burrs ranging from 8- to 12-cut by $\frac{3}{4}$ - to 5-in.

³³⁴ I. H. Andrews, S. A. Collicutt and R. C. Bedsoe, *Pulp Paper Mag. Canada* 47: 91-98, Convention Issue (1946)

lead.³³⁵ However, practically the same quality pulp can be produced by different burrs, depending upon the way they are used; for example, essentially the same grade of newsprint can be made by using a 14 diamond burr or a 10-1½ special burr.

Burrs come in different degrees of fineness, which is usually expressed in terms of the number of ridges, threads, or points per inch. The proper coarseness of the burr depends upon the type of stone, species of wood to be ground, the amount of available power and pressure to be used in grinding, and the freeness desired in the pulp. The coarser burrs are generally used on the soft stones with coarse grit. The finer burrs are often used in the summer months to slow up the stock. Sometimes the stock leaving the

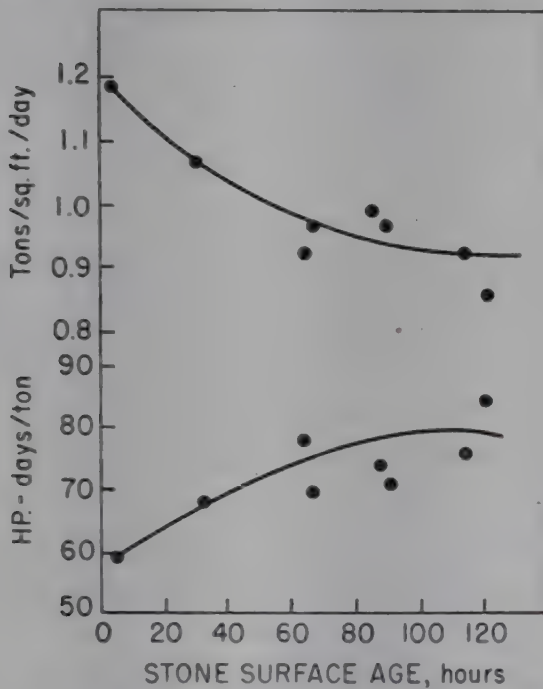


Fig. IV-23. Effect of stone surface age on production and power consumption (Roberts Grinder).

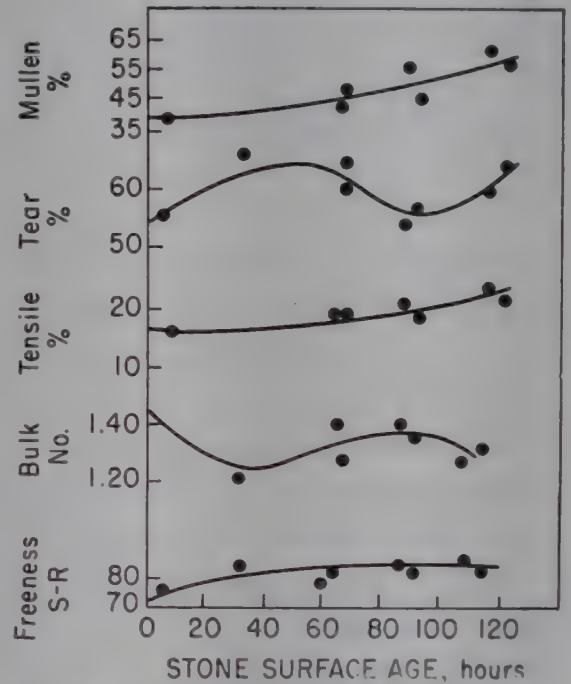


Fig. IV-24. Effect of stone surface age on properties of groundwood pulp (Roberts Grinder).

grinder immediately after burring is too coarse, in which case it may be necessary to dull (knock back) the stone by holding a very fine burr or a brick against the stone. An important factor in burring is the amount of pressure applied, since this determines the depth of the markings on the stone surface; excessively deep burring results in a high percentage of shives, which increases the waste. The pulp produced immediately after burring is of poor quality, but as grinding continues, the quality gradually improves.

As the stone surface wears away, production decreases, unit energy consumption increases, freeness decreases, and bursting strength increases. Thus, although strength increases with continued wear on the stone, too

³³⁵ H. J. Perry, *Pulp Paper Mag. Canada* 50, No. 5: 94-97 (Apr., 1949)

much wear cannot be tolerated from the standpoint of production and energy consumption. To offset wear, the stone must be resharpened at intervals, but burring must not be excessive, since this lowers the strength of the pulp and increases the amount of screenings. The schedule of burring must be so arranged that the interval between sharpenings is as uniform as possible in order that the properties of the pulp do not undergo abrupt and radical change. As a rule, the stone is reburred when the freeness and production have dropped below a predetermined value, which is usually a period of about 75 to 200 hours for artificial stones. Magruder³³⁶ has studied the effect of stone surface age on grinding rate, power consumption per ton, and pulp properties, using the Roberts grinder. The results are reproduced in Figures IV-23 and IV-24, from which it can be seen that a burring cycle of about 80 hours is optimum, since beyond this point power consumption and production are affected adversely. Natural stones may require sharpening about every 8 hours.

Stone Speed

Older mechanical pulp mills were operated with water wheels, but modern grinders are generally driven by constant speed synchronous motors on which a constant predetermined load is maintained by varying the pressure of grinding. Variations in pressure on grinders driven by water wheels result in a fluctuation in stone speed, but similar fluctuation does not occur on motor-driven grinders. Rotational speeds in pocket grinders vary from 200 to 275 r.p.m. Surface speeds for natural stones vary from 2,800 to 3,500 f.p.m. The average speed with artificial stones is about 4,000 f.p.m., but speeds up to 5,000 to 6,000 f.p.m. are practical.^{337, 338}

For normal grinding operations, production and power input to the grinder are directly proportional to stone speed. Energy consumption is generally not appreciably affected by stone speed,³³⁹ although in certain ranges energy consumption is decreased by increasing stone speed.³⁴⁰ Pulp strength is generally reduced by increasing stone speed.

Grinding Pressure

Grinding pressure has an important effect on the grinding characteristics of the wood and the physical properties of the final pulp. In general, increasing the grinding pressure increases the production, increases the power input to the grinder, and decreases the energy consumption (see

³³⁶ R. S. Magruder, *Tappi* 32, No. 1: 29-35 (Jan., 1949)

³³⁷ H. J. Perry, *Pulp Paper Mag. Canada* 50, No. 5: 94-97 (Apr., 1949)

³³⁸ H. J. Perry, *Tappi* 32, No. 2: 67-70 (Feb., 1949)

³³⁹ J. Edwards, G. D. O. Jones, G. J. Potter and H. W. Johnston, *Tech. Assoc. Papers* 20: 201-208 (June, 1937)

³⁴⁰ W. Brecht, *Papier-Fabr.* 33, No. 13: 119; 33, No. 14: 121; 33, No. 15: 129 (1935)

Fig. IV-25). The effect on pulp properties is to increase the freeness, decrease the strength, and increase the numbers of slivers. As the stone becomes dull through grinding, increased pressure is required to maintain a predetermined rate of grinding and freeness of the pulp. To prevent loss in production, the stone is reburred whenever the freeness falls below a certain level. For a given energy consumption, high pressure will generally produce a stronger pulp than low pressure. In commercial operation, grinding pressure is generally confined to a fairly narrow range, the upper limit of which is established by the available power.

Grinding pressure is a difficult calculation to make because of the variation in pressure between the wood and stone during grinding resulting from the change in the area of wood in contact with the stone as the wood is ground away. In the case of pocket grinders, unit pocket pressure can be calculated from the length of the wood, width of the pocket, cylinder pressure, and the diameter of the cylinder,³⁴¹ but calculation for the continuous type grinders is not so simple. Pocket pressures vary from 25 to 100 p.s.i.^{337, 342} Average operating pressure is probably in the neighborhood of 50 to 60 p.s.i., but best quality pulp is obtained at an average pressure of about 35 p.s.i. Newsprint is generally made in the range of low pressure, whereas groundwood for wallboard is made at high pressure.

In the early grinders, which were water-wheel driven, it was necessary to control the speed of rotation to prevent bursting of the stone at high speeds. In modern electric-driven grinders, speed control is not a problem, but power control is necessary to prevent excessive power swings. Control was first attempted by use of current-control governors (ammeters) and was followed later by wattmeter-controlled and resistance-controlled master governors. Governors regulate the speed of the driving chain in continuous grinders and regulate the hydraulic pressure on the pressure foot in intermittent grinders. Thus, in the case of pocket grinders, when one pocket is backed off for filling, more pressure is automatically applied to the remaining cylinders to maintain a constant total load on the motor. The process is then reversed when the pocket is refilled and is again grinding. This method of operation means that pulp quality is being sacrificed to greater power efficiency, but for practical purposes, the effect on pulp quality is not important.

Power Input

Power input to the grinder increases directly with grinding pressure. In practice, power input is widely used in place of pressure for controlling grinder operation because it is easier to measure power input than to meas-

³⁴¹ See TAPPI Data Sheets

³⁴² H. J. Perry, *Pulp Paper Mag. Canada* 50, No. 5: 94-97 (Apr., 1949)

ure specific pressure. Power input per unit of grinding surface can be calculated from the total power input per line and the projected grinding area of the pockets. The effect of power input on the production and consumption of power in the Roberts grinder is shown in Figure IV-25.³⁴³

The power required in grinding is determined by the species and density of the wood, type of pulp being made, condition of the stone surface, grinding pressure, speed of the stone, and temperature and consistency of stock in the grinder pit. For the same wood and constant condition of stone face and grinding temperature, power input can be calculated from

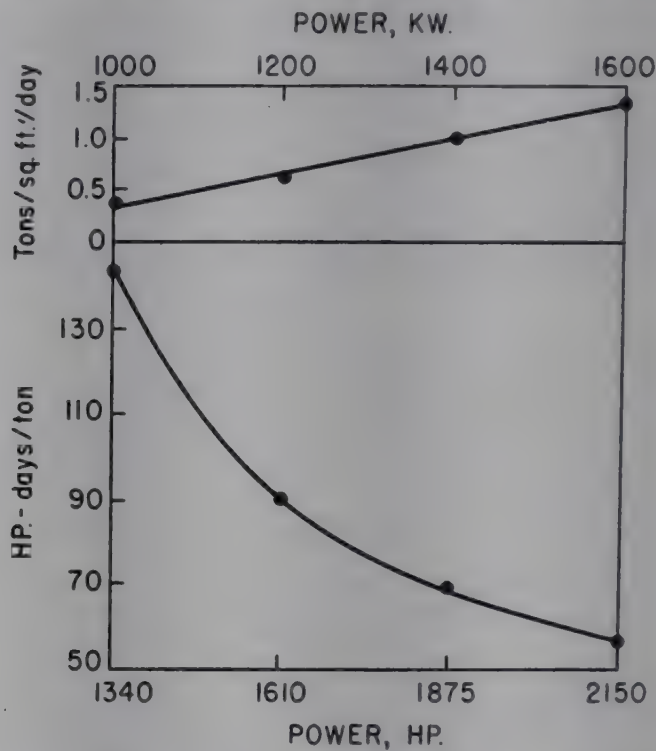


Fig. IV-25. Effect of power input on production and power consumption (Roberts grinder).

the applied pressure, peripheral speed of the stone, and the coefficient of friction between the wood and the stone surface, using the formula below.

$$\text{Total hp. delivered to grinder} = \frac{uW}{330,000} \times \frac{\pi dN}{12}$$

where u = coefficient of friction
 W = total thrust of pressure foot against stone in pounds
 d = diameter of stone
 N = r.p.m. of stone

In this formula, uW equals the force opposing rotation and $\pi dN/12$ equals the lineal velocity of the stone in feet per minute. The coefficient of friction for grinding varies from about 0.13 to 0.16 for commercial grinders to about 0.22 to 0.38 for miniature grinders.³⁴⁴

³⁴³ R. S. Magruder, *Tappi* 32, No. 1: 29-35 (Jan., 1949)
³⁴⁴ J. Edwards, G. D. O. Jones, G. J. C. Potter and H. W. Johnston, *Pulp Paper Mag. Canada* 38, No. 2: 121-132 (Feb., 1937)

The properties of the pulp vary appreciably with changes in power input for a given stone surface. The properties of pulp can also vary widely with constant power input to the stone, but this is always accompanied by a variation in the production of pulp due to changes in stone surface.

The bursting strength of the pulp decreases rapidly with increasing power input while the tear and tensile show little change except at the extremes, and bulk tends to increase linearly. Typical results are shown in Figure IV-26 taken from work by Magruder,³⁴⁵ on the Roberts grinder. (The bulk number is reported as the caliper of eight sheets divided by 8, the result divided by the basis weight, and this result multiplied by 10.) High

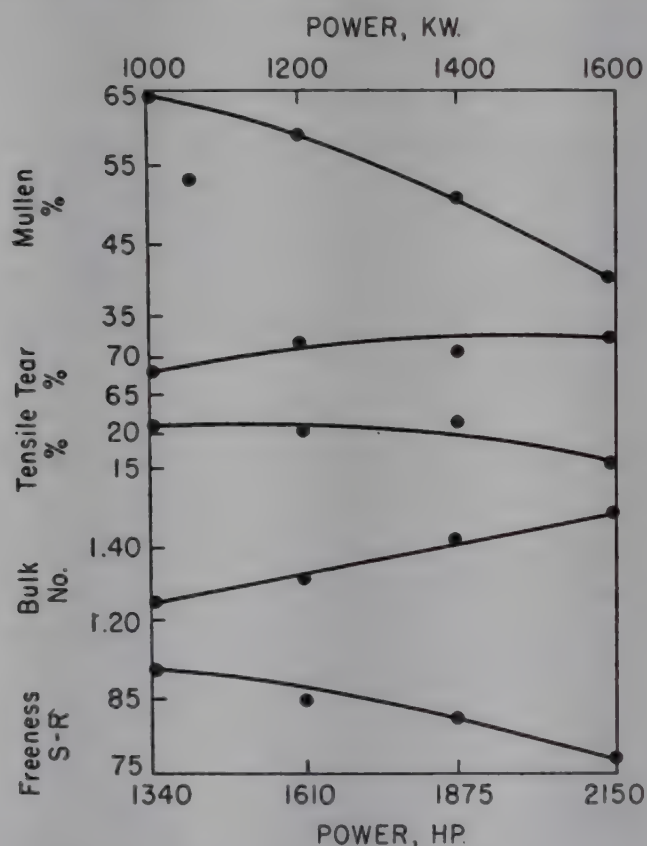


Fig. IV-26. Effect of power input on properties of groundwood pulp (Roberts grinder).

strength and low bulk are obtained at low power input, but this is the point where production is low (see Fig. IV-25).

Energy Consumption

Energy consumption in mechanical pulping is one of the most important grinding characteristics. Energy is usually expressed in horsepower-days per ton of air-dry pulp produced and is calculated by dividing the horsepower input to the grinder by the tons of pulp produced per day. Pulp strength and energy consumption are closely related variables. For a given stone surface, the strength of groundwood increases directly with an in-

³⁴⁵ R. S. Magruder, *Tappi* 32, No. 1:29-35 (Jan., 1939)

crease in the amount of energy consumed in grinding. A relatively fixed amount of energy is required to produce a particular grade of pulp from a given species of wood. Sometimes energy consumption and pulp strength are expressed in one factor combining energy consumption per ton of pulp per meter of breaking length.³⁴⁶

The energy supplied to the stone in grinding is consumed in overcoming the friction between the stone and the surface of the wood. Practically all the energy consumed reappears as sensible heat in the grinding water; only a very small amount of energy is absorbed in forming new surfaces, owing to fibers being separated from the wood.³⁴⁷ Power consumption runs from about 55 to 66 hp. per ton for hanging (wallpaper) stock, 60 to 70 hp. per ton for newsprint, and 80 hp. per ton or over for book grade groundwood, using spruce.

Energy consumption in grinding decreases with an increase in stone sharpness, an increase in pressure, or an increase in stone speed. The horsepower consumption of continuous grinders can be reduced by operating at low pit consistency (e.g., 2 to 2½%), with low stone submer-sion, and by better cleaning of pulp from the surface of the stone.

Production

The production of pulp is a variable of obvious importance in mechanical pulping. Production may be calculated as tons of air-dry pulp produced per grinder per 24 hours, or as tons of pulp produced per square foot of grinding surface per day. The latter is obtained by dividing the tons of pulp produced per day by the pocket area in square feet. Values for the grinding of spruce in pocket grinders vary from 0.6 to 1.8 tons per square foot per day.

Production increases with increase in stone sharpness, increase in grinding pressure, or increase in stone speed. With constant power input, the only way production can be increased is by sharpening the stone, which increases the production per unit of grinding surface. In general, bursting strength decreases with increasing production, and freeness increases with increasing production.

Temperature of Grinding

The effect of temperature on grinding is of recognized importance. The temperature which is important is the working temperature at the wood-stone interface, but in commercial practice, it is customary to measure the temperature in the grinder pit, or of the stock on the discharge side of the stone, where the temperature is usually lower than the working tem-

³⁴⁶ J. H. Thickens, U. S. Dept. Agr. Bull. 127 (1913)

³⁴⁷ J. Edwards, G. D. O. Jones, G. J. Potter and H. W. Johnston, *Tech. Assoc. Papers* 20: 201-208 (June, 1937)

perature.³⁴⁸ The amount of heat generated varies with the pattern on the stone, the density of the wood, and the pressure applied. Grinder pit temperature can be controlled at the desired point by regulating the amount of shower water or extra white water added to the grinder pit.

There are, in reality, two types of grinding processes, known as hot grinding and cold grinding. Nearly all grinding in the United States and Canada is hot grinding, that is, the temperature of grinding is in the range of 135° to 190° F. and the consistency in the range of 2 to 8%. The cold grinding process, which is used mostly in Europe, employs larger quantities of water, and the consistency of the pulp in the grinder pits is correspondingly lower, about 2 to 4%.

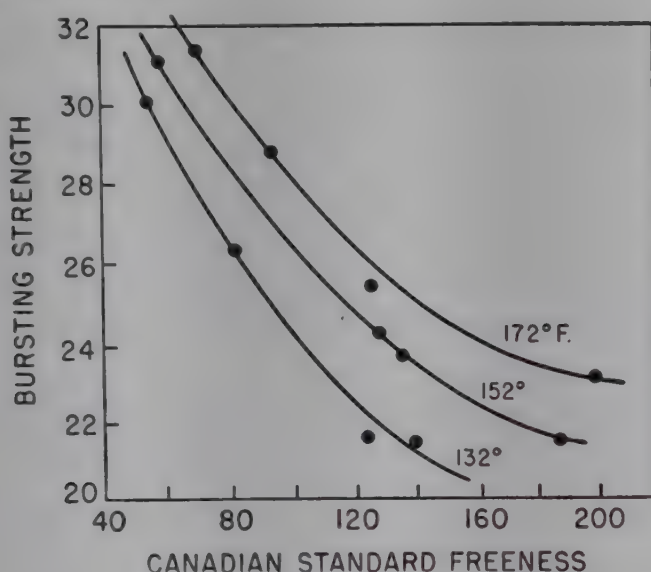


Fig. IV-27. Effect of temperature of grinding upon bursting strength.

Variation in grinding temperature affects the freeness, color, and strength of groundwood, and has an influence on the rate of production and amount of energy consumed.³⁴⁹ Increasing the temperature (at constant consistency) increases the grinding rate, decreases the energy consumption, increases the freeness, and increases the pulp strength,³⁵⁰ although the influence of temperature in ordinary grinding is rather small. In general, hot grinding produces a strong fiber, whereas cold grinding produces a fine stock of low freeness. At least part of the beneficial effect of high temperature on grinding can be attributed to the reduced viscosity of the water.³⁵¹ Magruder³⁵² found, with the Roberts grinder, that temperature had rela-

³⁴⁸ J. C. Jaeger and J. L. Somerville, *Paper Trade J.* 129, No. 11: 99-104 (Sept. 14, 1944)

³⁴⁹ C. D. Demars, *Pulp Paper Mag. Canada* 42: 378-379 (Aug., 1941)

³⁵⁰ E. R. Schafer and J. C. Pew, *Paper Trade J.* 101, No. 13: 167-172 (Sept. 26, 1935)

³⁵¹ E. R. Schafer and J. C. Pew, *Paper Trade J.* 105, No. 18: 266-268 (Oct. 28, 1937)

³⁵² R. S. Magruder, *Tappi* 23, No. 1: 29-35 (Jan., 1949)

tively little effect on pulp properties until the temperature was increased over 160° F., after which production rose sharply, tear and bulk increased, and bursting strength slightly decreased. Andrews³⁵³ obtained a progressive increase in bursting strength for constant freeness when the temperature was increased, as shown in Figure IV-27. The effect of temperature on the quality of pulp appears to be less as the speed of grinding is increased. In practice, temperatures as high as 190 to 200° F. are used, but it is generally believed that the most satisfactory pulp is obtained at temperatures of 155 to 165° F. It is desirable to maintain the maximum temperature consistent with the quality of pulp desired.

Consistency of Grinding

Uniform temperature is obtained in commercial grinding at the expense of uniform consistency because of the fact that temperature is generally controlled by regulation of the amount of cooling water used in the showers. For this reason, it is difficult to separate the effects due to temperature from those due to consistency, and ordinarily no attempt is made to do so. Pit consistencies are generally about 3 to 4%, although pit consistencies as high as 8 to 9% are sometimes used. As a rule, increasing the consistency of the pulp in the grinder pit above 4% results in an increase in the energy consumption and a decrease in the grinding rate.³⁵⁴ For increases in the pit consistency between 1 to 10%, Andrews³⁵⁵ obtained the results below:

	For constant grinding pressure	For constant freeness
Production	Decreases	Increases
Freeness	Decreases	
Burst	Increases	Decreases
Energy consumption	Increases	Increases

Freeness and Strength

Bursting strength and freeness (Canadian Standard and Schopper-Riegler) are the two classical means of measuring the quality of groundwood, although fiber classification is often used. Groundwood pulps produced by the same grinder from the same wood under unchanging operating conditions show a definite relationship between freeness and bursting strength. This relationship is exponential in nature, i.e., a plot of burst and freeness on semi-log paper is a straight line, as shown in Figure IV-28.^{356, 357} Assuming that the curve in Figure IV-28 denotes average

³⁵³ H. Andrews, *Pulp Paper Mag. Canada* 41: 89-90, Convention Issue (1940)
³⁵⁴ E. R. Schafer and J. C. Pew, *Paper Trade J.* 101, No. 13: 167-172 (Sept. 26, 1935)
³⁵⁵ H. Andrews, *Pulp Paper Mag. Canada* 42, No. 2: 117-120 (Feb., 1941)
³⁵⁶ R. I. Wynne-Roberts, *Tech. Assoc. Papers* 20: 258-260 (June, 1937)
³⁵⁷ H. A. Paterson, *Pulp Paper Mag. Canada* 37: 79-80, 126 (Feb., 1936)

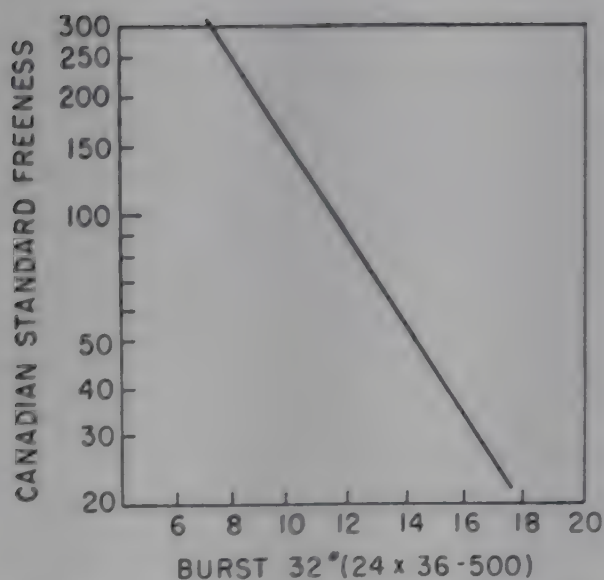


Fig. IV-28. Relation of freeness to burst.

quality, then a shifting to the right signifies improved quality and a shifting to the left signifies lowered quality.

By the use of curves such as those shown in Figure IV-29, ground-wood pulps of different freeness and strength values can be compared on a common basis by bringing to a common freeness (usually 100 cc.) or to a

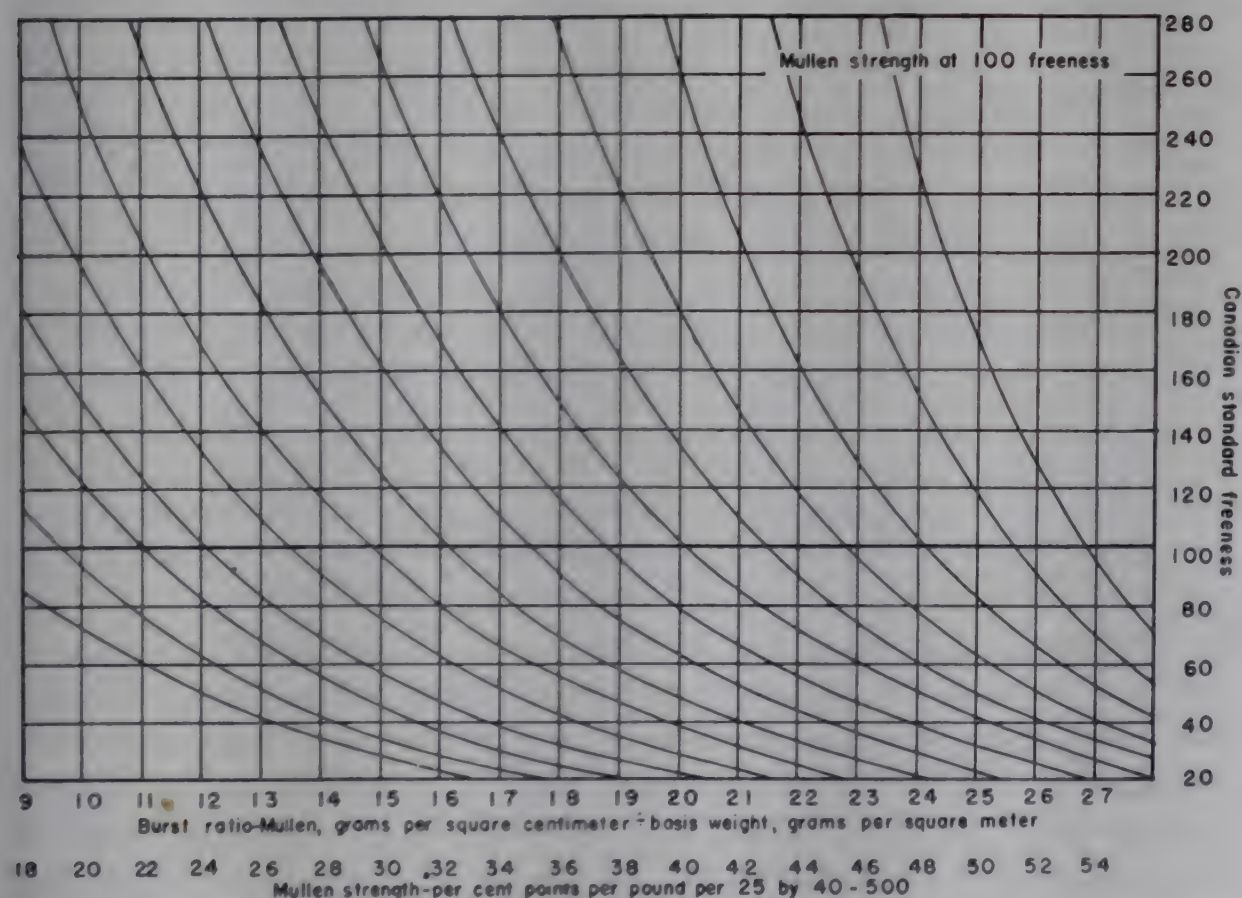


Fig. IV-29. Chart for converting from burst at one freeness to equivalent burst at a different freeness (TAPPI Data Sheet 34B, courtesy Technical Association of the Pulp and Paper Industry).

common bursting strength. For example, the strength of groundwood of any given freeness may be converted into strength corresponding to any standard freeness, such as 100 cc., by finding the curve which most closely corresponds to the given freeness and bursting strength, and then following that curve to the corresponding strength at freeness 100 cc. The curves in Figure IV-29 are useful for comparing the effect of wood, grinder stones, and process variables on the quality of product. The curves hold fairly well for most conditions, but specific curves may be necessary where a high degree of accuracy is required.

For a given species, bursting strength varies in a definite relationship with freeness, and both of these properties of the pulp are determined by

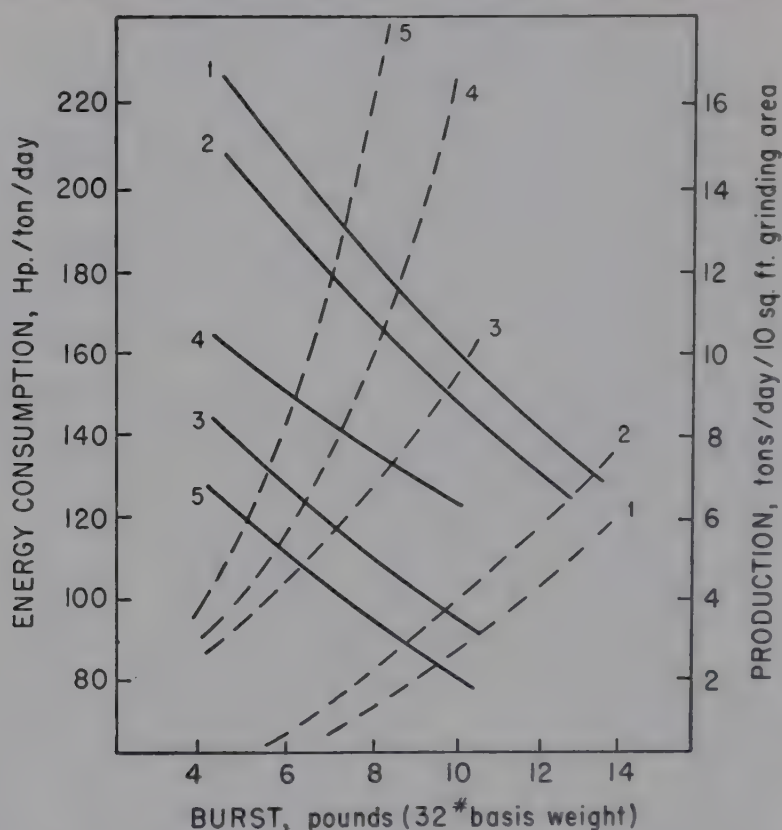


Fig. IV-30. Relation between bursting strength, energy consumption (---), and production (—) in grinding of different woods: (1) spruce; (2) balsam; (3) shortleaf pine; (4) poplar; (5) cottonwood.

the conditions of grinding. If increased strength (reduced freeness) is desired, it is necessary to supply more unit energy to the pulp. This, in turn, reduces the rate of production if all other conditions are unchanged. On the other hand, if the production is increased, keeping the unit energy constant, the pulp strength will decrease and the freeness will increase. These effects are shown in Figure IV-30, where production and energy consumption are plotted against bursting strength for several different species of wood.³⁵⁸

³⁵⁸ R. I. Wynne-Roberts, *Tech. Assoc. Papers* 20: 258-260 (June, 1937)

Wood Variables

The important wood variables affecting the grinding characteristics of the wood and the quality of the mechanical pulp are species, density, and moisture content. The desirable characteristics of wood for mechanical pulping are good color, a high degree of softness (low density), and long fibers. For best results, each species should be ground separately to permit the optimum grinding conditions for that species.

Softwoods are generally preferred for mechanical pulping, although hardwoods, especially aspen, have enjoyed an increasing use in recent years. Spruce and balsam are the most desirable species because of their low energy consumption in grinding and their high production rates. In the northern states and Canada, spruce is widely used, together with smaller amounts of jack pine, balsam, hemlock, white fir, and tamarack. Spruce and balsam are rather similar in grinding properties, although less power is required with spruce, and the resulting pulp produces a harder sheet than balsam. Hemlock groundwood has a shorter fiber length than spruce groundwood, and the color is slightly reddish. In the southern states, increasing quantities of pine are being used. Coarse-grained stones are required for southern pines, compared with the stones used on spruce, to produce uniformly long-fibered pulp. The energy consumption per ton of pulp is generally 20% or more higher than that required for spruce of comparable quality. Jack pine has a limited use in the northern states, but it, too, requires higher energy consumption than spruce, and the wood is knotty. The pulp is resinous and poor in color and has a lower strength than spruce for a given freeness. It had been stated that more than 15% jack pine in a groundwood furnish increases the likelihood of pitch trouble on the paper machine.³⁵⁹ On the West Coast, spruce (Sitka and Engelmann) and the true firs are preferred, although hemlock is used.

The grinding characteristics of a few different species are shown in Table XVII, where it can be seen that spruce and balsam do not require as high an energy consumption as poplar or the pines and the pulps produced have a higher freeness for a given bursting strength.³⁵⁸ The values for energy consumption given in Table XVII are not exactly comparable with commercial values because of the low grinding pressure used (20 p.s.i. of pocket area), but the values serve for comparing one wood with another.

Under ordinary grinding conditions, hardwoods (aspen) grind at a higher rate and consume less energy per ton than spruce, but the pulp obtained is much lower in strength.³⁶⁰ Strength can be greatly improved by increasing the energy consumption through use of a dull stone surface, but this increases the cost by sacrificing production and power. Aspen is the

³⁵⁹ K. D. Running, *Pulp Paper Mag. Canada* 42: 104-106 (1941)

³⁶⁰ E. R. Schafer and A. Hyttinen, *Tappi* 33, No. 7: 335-337 (July, 1950)

TABLE XVII

GRINDING CHARACTERISTICS OF DIFFERENT WOODS
[Bursting strength constant at 8 p.s.i. (32 pound basis weight)]

Species	Freeness, cc.	Production, tons/10 sq.ft./day	Power consumption, Hp./ton/day
Spruce	115	12.0	70
Balsam	68	9.6	80
Hemlock	40	7.4	108
Jack pine	58	8.0	105
Shortleaf pine	42	6.4	125
Poplar	37	6.0	140
Loblolly pine	25	4.8	150
Cottonwood	22	3.2	215

most satisfactory of the hardwoods, and appreciable amounts of native aspen are ground in the United States, while a hybrid species grown as a crop is used in Italy.³⁶¹ The pulp from aspen compares favorably in color with spruce and balsam groundwood. The strength of the pulp is nearly equal to that of spruce groundwood, but, as mentioned above, the energy consumption is higher. Typical results obtained on a laboratory grinder (32-in. diameter, 11-in. face) are as follows:³⁶²

Species	Burst, points per pound	Energy consumption, hp.—day per ton
Spruce	0.28	65
Aspen	0.22	75

If a relatively bulky stock is desired, aspen can be ground with a fairly sharp stone at low energy consumption.

Density of the wood appears to be the most important factor in grinding, since pulps produced from the high-density hardwoods are uniformly

TABLE XVIII •

RELATION OF YIELD TO DENSITY IN GROUNDWOOD PULPING

Species of wood	Density, oven-dry weight on green volume	Yield of screened pulp per cunit
Loblolly pine49	3000
Shortleaf pine46	2850
Cottonwood44	2700
Poplar43	2575
Jack pine41	2500
Hemlock (eastern)40	2450
Spruce38	2375
Balsam34	2050

³⁶¹ J. E. Atchinson, *Tappi* 33, No. 2: 20A, 22A, 24A, 26A, 28A, 30A (Feb., 1950)
³⁶² C. E. Libby and F. W. O'Neil, *Tappi* 33, No. 4: 161-178 (Apr., 1950)

low in strength and poor in color. High-density hardwoods (e.g., birch, beech, and maple) produce pulps having less than 25% of the strength of spruce groundwood. These high-density hardwoods are of interest, since they yield from 25 to 30% more pulp per cord than spruce or the low-density hardwoods, and the energy consumption is less, but the low strength and poor color have limited their use. Yield of pulp and density of wood bear an approximate linear relation to each other, as shown in Table XVIII.³⁶³

As a general rule, fresh wood which is still slightly moist grinds more easily and produces longer fibers than wood which is seasoned and dried. The moisture content of the wood at the time of grinding should be 40 to 45% or higher for best results, since the strength of the pulp drops off if the moisture content is much below this value. Grinding of dry wood (i.e., moisture of 30% or less) produces a stubby, soft stock, containing a high percentage of fines. If the moisture content is increased and the grinding pressure held constant, production is increased and energy consumption is decreased. On the other hand, if the moisture content is increased and the pressure adjusted to maintain constant freeness, production is decreased and the energy consumption is increased.³⁶⁴

Characteristics of Groundwood Pulp

Groundwood pulp does not contain morphological fiber entities, but instead the pulp is composed of individual fibers, broken fibers, fines, and coarse fiber bundles. The quality of the fiber in groundwood can be determined in qualitative fashion by placing a small quantity of dilute stock on a blue glass plate set in a wooden frame and examining the contents against a strong light. The glass is covered to a depth of about 1/16 in., with stock at about 0.05% consistency. Since the light is blue and the fibers white, the nature and uniformity of the fibers show plainly. In the hands of an experienced person, the test will show something about the ease of clotting, number of shives, number of fines, and the average length of the fibers. A quantitative evaluation of the pulp can be made by means of a microscopic examination or by putting the pulp through a fiber classifier to determine the proportion of fiber of different fiber lengths (see Chapter VI, Fiber Preparation). The amount of fiber "fines" (the portion of the pulp passing a 150-mesh screen) is usually from 40 to 60% of the pulp.

The ray cells in the wood are usually ground finer than the wood fibers because of their orientation relative to the stone during grinding, and because of their smaller size and thinner walls. Much of the coloring matter contained in the ray cells is set free in grinding in the form of finely divided

³⁶³ R. I. Wynne-Roberts, *Tech. Assoc. Papers* 20:258-260 (June, 1937)

³⁶⁴ W. S. Morris, *Pulp Paper Mag. Canada* 44: 501-508 (June, 1943)

particles which tend to segregate in the sheet during formation.³⁶⁵ The presence of coloring matter causes considerable trouble in some ground-wood pulps; for example, groundwood from certain of the western woods of the United States (e.g., western hemlock) has a decidedly pink color. On the other hand, certain hardwoods, such as basswood and sycamore, produce very bright pulps, due to their lack of coloring matter. Sometimes a small percentage of these last-mentioned woods is used for the express purpose of increasing the brightness of the pulp. Improved methods of bleaching groundwood have been developed recently.

Groundwood is low in strength compared with sulfite and sulfate pulps. The pulp does not "hydrate" in beating, but instead tends to break up, thus producing bulky papers. Because groundwood contains practically the whole wood, papers made from groundwood deteriorate rapidly in strength and turn yellow on aging. For this reason, groundwood is used only in relatively impermanent papers such as newsprint, cheap book, catalogue, rotogravure, magazine, cheap drawing, toilet tissue, toweling, hanging stock, coating raw stock, and some grades of wallboard and paperboard. For these grades, groundwood has the desirable properties of low cost, good printing quality, and high opacity. Printing qualities are good because of the high bulk, high smoothness, resiliency, and good ink absorption. The particular properties required for a given grade of paper are obtained by selection of the proper species and regulation of the grinding conditions; for example, groundwood to be used in book papers is ground in such a way that the fiber is short and fine, whereas groundwood for catalogue is ground in a way to produce a longer-fibered stock. Coarse groundwood has a higher freeness and produces bulkier paper than fine groundwood.

The amount of groundwood used in newsprint and hanging stock is about 85% of the fibrous furnish. Groundwood is used in printing papers to the extent of 30 to 70% of the fibrous furnish. Other grades of paper may contain from 10 to 100% groundwood. A small amount of groundwood (up to 10 to 20%) in mixture with long-fibered chemical stock will generally increase the bursting strength of the paper slightly without lowering the tearing resistance, owing to the groundwood filling in between the longer fibers of the chemical pulp. Higher percentages of groundwood materially lower the strength of the paper. Hardwood groundwood generally has a lower strength than spruce groundwood, although this depends upon the species and the method of grinding the wood. Aspen groundwood has been used up to about 15% of the furnish in newsprint and up to 50% of the furnish in printing papers without harm to the paper. On the other

³⁶⁵ C. E. Curran, E. R. Schafer and J. C. Pew, *Paper Trade J.* 101, No. 8: 91-97 (Aug. 22, 1935)

hand, Sears³⁶⁶ found that over 10% birch groundwood reduced the strength of newsprint materially.

Mechanical Pulp from Pretreated Wood

Ever since the invention of the groundwood process, there has been considerable interest in methods of reducing the power requirements and improving the quality of the pulp. Among the early processes which attracted considerable attention were the Hall process, in which the wood was subjected to boiling water before grinding, and the Enge process, in which the wood was heated in water at 230 to 257° F. for 5 to 10 hours at a pressure higher than the steam pressure at that temperature. Soluble organic acids are formed when wood is treated in this way, and there is some depolymerization of the cellulose,³⁶⁷ but the principal effect is a softening or partial solvent action on the lignin in the wood which renders the wood more easily separable into fibers. The result is a pulp which has a higher freeness and a greater strength and stiffness than regular groundwood. The pulp is dark colored, however, and this limits its use to paperboards and cheap grades of brown paper.

Steaming of wood is not widely practiced today, but the process has some merit particularly for the hardwood species, which, generally do not discolor as much as the softwoods. One beneficial effect of steaming is reduced trouble with pitch. The energy consumption per ton of steamed groundwood is about 25% higher than that of regular groundwood. Increasing the degree of treatment by increasing the time or temperature of steaming increases the strength, lowers the yield, and lowers the color of the pulp, while the energy consumption is slightly increased.

In more recent times, attempts have been made to improve the strength and fiber length of groundwood by treatment of the wood with chemicals. Two different processes have been proposed: (1) treatment of the wood at the time of grinding by introducing chemicals in the grinding water and (2) pretreatment of the log at high temperature and pressure before grinding. The former process has little to recommend it. Processes for pretreating the wood before grinding were suggested years ago, but they, too, never attained any practical importance, principally on account of the difficulties in obtaining uniform softening of the log, and because the process was tried mostly on softwoods, which are not well suited to this type of treatment.³⁶⁸ One of the early processes (Hall process) for pretreating wood used alkaline liquors, e.g., sodium hydroxide, sodium sulfite, sodium bisulfite, sodium

³⁶⁶ L. G. Sears, *Pulp Paper Mag. Canada* 46, No. 3: 185-186, Sixth Wartime Issue (1945)

³⁶⁷ S. Coppick, *Paper Trade J.* 117, No. 26: 269-271 (Dec. 23, 1943)

³⁶⁸ J. D. Rue, *Paper Trade J.* 81, No. 16: 157-159 (Oct. 15, 1925)

sulfide, and sodium carbonate, but these alkaline liquors caused considerable darkening of the wood, and the pulps were not suited to the manufacture of white papers. Another process (Decker process) used sulfur dioxide as a means of improving the color of the pulp,³⁶⁹⁻³⁷¹ but the acid liquors caused trouble with corrosiveness. More recent work at the New York State College of Forestry has shown that pretreatment before grinding results in an excellent pulp when hardwoods are used. Neutral sulfite liquor containing sodium sulfite plus sodium bicarbonate was found to be the most satisfactory treating liquor.

The pulp produced by pretreatment of hardwoods before grinding has been given the coined name, "chemigroundwood."³⁷² The pulp is unique for groundwood, since there is uniform separation of the woody tissues, the typical fiber bundles and broken fibers of ordinary groundwood being entirely absent. The strength of the pulp is excellent, being three to four times as strong as regular spruce groundwood. The power requirements in grinding are about one-half to two-thirds those of spruce groundwood, and the production rate is about double. These advantages, plus the fact that the dense hardwoods can be used and the yield maintained at 85 to 90%, gives this process a tremendous economic advantage over the regular grinding of spruce.

The one disadvantage of the chemigroundwood process is the low brightness of the pulp. Even with aspen, a normally bright wood, dark-colored pulps are usually obtained. The low brightness is believed to be caused by infected areas in the heart of the wood, known as "wet wood." These areas are difficult to penetrate because the vessels in the affected region are closed by barriers which prevent the movement of the treating liquor. The pulp responds readily to bleaching, and brightness gains of 7 to 15 points can be obtained with 2% peroxide, or 10% available chlorine added as hypochlorite. However, because of the lower initial brightness, bleached hardwood chemigroundwood is only slightly brighter than unbleached spruce groundwood. However, recent operating improvements have shown how the original brightness of the unbleached pulp can be improved.

Several processes have been proposed for the manufacture of pretreated groundwood. Longhead³⁷³ has described a commercial process in which the wood in log form is treated in an autoclave with a solution of sodium sulfite and sodium bicarbonate in a ratio of 7 to 1 at a temperature of 115 to

³⁶⁹ *Paper* 17, No. 21: 18 (Feb. 2, 1916)

³⁷⁰ *Paper* 18, No. 6: 19 (Apr. 1916)

³⁷¹ C. G. Schwalbe, *Paper Mill* 28, No. 44: 32-34 (Oct. 30, 1915)

³⁷² C. E. Libby and F. W. O'Neil, *Tappi* 33, No. 4: 161-178 (Apr., 1950)

³⁷³ E. H. Longheed, *Pulp Paper Mag. Canada* 46, No. 3: 165-175, Sixth Wartime Issue (1945)

125° C. for 2½ to 4½ hours, and a pressure about 60 p.s.i. higher than the saturated steam pressure. About 7 lb. of liquor per ton of wood is used for the treatment or, in other words, enough to keep the final pH of the liquor at 7.2 to 7.4. A four-cycle process for pretreating hardwoods with neutral sulfite liquor before grinding has been proposed by the Forest Products Laboratory.³⁷⁴ In this process, the wood is submerged in a liquor consisting of 60 g./l. of sodium sulfite and 20 g./l. of sodium bicarbonate and then subjected to (1) a half-hour vacuum treatment, (2) heating to 250° F. at a pressure of 140 p.s.i. for a half-hour, (3) vacuum for another half hour, and (4) finally heating again at a temperature of 250° F. and a pressure of 140 p.s.i. for a half-hour. The pressure is then relieved, the liquor is drained, and the wood is ground within 2 hours.

Extensive work on chemigroundwood pulp has been done at the New York State College of Forestry in an effort to establish optimum operating conditions. Investigation of different cooking liquors established the most satisfactory cooking liquor (for aspen, birch, beech, and maple) as one containing a ratio of 6 parts of sodium sulfite to 1 part of sodium bicarbonate. Higher ratios of sulfite to bicarbonate resulted in lower energy consumption in grinding and higher brightness pulp, but the strength of the pulp was lowered. The optimum concentration of chemical for impregnating 4-ft. logs was found to be 1.5 lb./gal. These concentrations of chemical established a pH of 9.3 to 9.5 during the cooking period. After loading the logs in the digester, cooking conditions were established by evacuating the digester for about 30 minutes, raising the temperature to 140 to 150° C. by admitting steam to an outside heat exchanger, applying hydrostatic pressure (120 p.s.i.) to raise the overall pressure level to 200 p.s.i., and holding under these conditions for 6 hours. Temperatures over 150° C. or treating periods over 6 hours were found to reduce the strength of the pulp. Lowering the temperature and pressure in the later stages of the cook has the advantage of producing a lighter colored pulp.

At the end of the cook, the free liquor can be blown to a storage tank and the treated wood removed for grinding. Optimum grinding was obtained at a grinder pit temperature of 130° F. and a pocket pressure of 40 p.s.i. The consumption of chemical by the wood when treated in the above manner was about 10% of the dry weight of the rawwood. Free liquor recovered from the cook can be reused repeatedly when fortified with fresh chemical without harm to the color or strength of the pulp.

WHOLE WOOD FIBER MANUFACTURE

Whole wood fiber manufacture may be defined as the reduction of wood to a fibrous state without chemical action on the wood and without appre-

³⁷⁴ A. Hyttinen and E. R. Schafer, *Tappi* 32, No. 2: 79-85 (Feb., 1949)

ciable delignification so that the final product has essentially the same composition as the original wood and the yield is close to 100%. Groundwood pulps are essentially whole wood fibers. Other processes producing whole wood fibers are discussed below.

Whole wood fiber is generally made from untreated wood in the green condition or from wood which has been treated with steam or hot water. Steaming softens the wood, weakens the bond between the fibers, and produces a pulp containing fewer broken fibers. This generally reduces the power consumption required for defibering, but lowers the color and yield of the pulp to a degree dependent upon the time and temperature of steaming. The amount of heat treatment given to the wood depends upon the species and the final product that is desired. With spruce, balsam, aspen, some of the pines, and a few other species, the wood may be defibered in the green and water-soaked condition without any pretreatment. Certain other species (e.g., Douglas fir, jack pine, and some of the yellow pines) required a presteaming treatment, or a very mild semichemical cooking. Certain of the hardwood species (e.g., birch and gum) cannot be satisfactorily reduced to the fibrous states without a fairly drastic semichemical treatment. In general, hardwoods are more affected by steaming than softwoods.

Pulps produced by the whole wood processes are suitable only for coarse wallboards, insulating material, saturating felt, and corrugating paper. The pulps make excellent insulating material because of their high thermal resistance, good felting qualities, high degree of resilience, high degree of toughness, good water resistance, and other desirable properties.³⁷⁵

Whole wood fiber can be formed into fiberboards using either special cylinder or fourdrinier type machines. After wet pressing, the board is cut into sheets 8 to 12 ft. wide and 8 to 24 ft. long and fed automatically into multiple-deck driers where the board is dried by means of steam coils at 250 to 400 p.s.i. In some cases, the board is dried in continuous form and then is cut into appropriate lengths at the end of the machine, using a special traveling saw. Certain mills on the West Coast use automatically controlled, vacuum-operated machines which form individual sheets 4 by 8 ft. in size. If hardboard is being made, the fibers are welded together by pressing the board at high temperature (e.g., 190° C.) and high pressures (700–800 p.s.i.). Heat-setting resins (e.g., phenolics) may be incorporated in the stock before hot pressing.

Whole Wood Fiber from Untreated Wood

Certain species of wood (e.g., aspen) are shredded in the green state (moisture content 30% or over) without pretreating the wood. A suitable

³⁷⁵ C. C. Heritage and T. C. Duvall, *Southern Pulp & Paper Mfr.* 11, No. 9: 50, 52–54, 56 (Sept. 15, 1948)

piece of equipment is the Allis-Chalmers Defiberizer, consisting of two cylinders to which are attached numerous small pointed hammers. The hammers swing freely on rods extending along the axis of the cylinders. When wood in log form is fed to the revolving hammers, the wood is literally "combed" into a fibrous state, the fibers being removed from the tangential surface of the bolt. Slabs and edgings can be used in place of bolts, but the yields of usable fiber is not so high. The final pulp consists mostly of fiber bundles and is coarser, stiffer, and bulkier than pulp obtained from wood pretreated with steam or chemicals before defiberizing.

Disk mills, either single rotary or double rotary, can be used for fiberizing green or water-soaked wood. The power consumption is approximately equal to the power consumption required in ordinary grinding to produce an equivalent quality pulp.³⁷⁶ The United States Forest Products Laboratory^{377, 378} has described a process (so far used only in the laboratory) in which green wood chips of Douglas fir $\frac{5}{8}$ to $\frac{3}{4}$ in. long and water (at 15° C.) are defiberized in a refiner of the double-disk type (Bauer Refiner). The chips are fed into the "eye" of the rotating disk, after which they are thrown by centrifugal force over the serrated faces of the disks where the chips are rubbed into a fibrous state. Energy consumption in the range of 40 to 60 hp-days/ton is required to obtain the strongest boards. A disadvantage is the low freeness derived from the fines in the stock.

Whole Wood Fiber from Steam- or Water-Treated Wood by Batch Process

The water cooking or steaming of chips in a batch process, followed by continuous refining in a disk mill, has been used for making whole wood fiber. Steam and water cooking appear to give about the same results, but steam cooking is generally preferred for commercial operation. In commercial operation, the treatment varies from a few minutes steaming at high pressure (100–300 p.s.i.) to several hours steaming at low pressure (25 p.s.i.). A pressure of 150 p.s.i. and a time of 45 minutes are considered adequate for extreme conditions,³⁷⁹ but valuable fiber can be prepared from some species by steaming for 15 minutes at 100 p.s.i.,³⁸⁰ and even for much shorter periods. If iron digesters are used for steaming, a small amount of alkali may be added to neutralize the organic acids produced by hydrolysis of the wood.

The effect of time and temperature variables on the water and steam

³⁷⁶ C. K. Textor, *Paper Trade J.* 126, No. 16: 47–53 (Apr. 15, 1948)

³⁷⁷ H. D. Turner, J. P. Hohf and S. L. Schwartz, *Paper Trade J.* 129, No. 9: 43–50 (Aug. 26, 1948)

³⁷⁸ S. L. Schwartz and P. K. Baird, *Paper Trade J.* 130, No. 24: 106–118 (June 15, 1950)

³⁷⁹ A. S. Holden, *Tappi* 32, No. 6: 259–264 (June, 1949)

³⁸⁰ C. K. Textor, *Paper Trade J.* 126, No. 16: 47–53 (Apr. 15, 1948)

cooking of aspen (*Populus tremuloides*) has been given considerable study.³⁸¹⁻³⁸³ The effect of temperature on yield of aspen when cooked for a constant time of 4 hours is shown in Table XIX,³⁸¹ where it can be seen that the greatest decrease in yield occurs between 100 and 148° C., after which the yield decreases in an orderly way with increasing temperatures from 150 to 180° C.³⁸⁴ There is a critical point beyond which wood should not be heated if substantial losses due to gasification are to be avoided.³⁸⁵ In the case of aspen, the critical point is obtained at steam pressure of 175 p.s.i. for 4 minutes' heating and 200 p.s.i. for 2 minutes' heating.

Short heating periods have little effect on yield unless temperatures above 150° C. are used,³⁸⁶ but above this, yield decreases fairly steadily with increasing time of heating. The effects of time of water cooking on

TABLE XIX

EFFECT OF TEMPERATURE ON YIELD OF ASPEN WHEN COOKED IN WATER FOR FOUR HOURS

Temperature, °C.	Yield, per cent of original wood
100	97.4
148	78.5
170	71.2
186	67.9

the yield and strength of pulp obtained from aspen is shown in Table XX³⁸⁶ for a constant cooking temperature of 170° C.

Maximum pulp strength is obtained at a yield of about 80 to 85%.³⁸⁷ The rate of solution of lignin and carbohydrates during cooking is practically the same down to a yield of about 75%, and consequently most pulps have roughly the same lignin content as the original wood, about 16.5% in the case of aspen.^{388, 389} A mild treatment for 2 hours at atmospheric

³⁸¹ S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.* 22, No. 3: 264-274 (Mar., 1930)

³⁸² C. C. Heritage and T. C. Duvall, *Southern Pulp & Paper Mfr.* 11, No. 9: 50, 52-54, 56 (Sept. 15, 1948)

³⁸³ J. N. McGovern, K. J. Brown and W. A. Kraske, *Tappi* 32, No. 10: 440-448 (Oct., 1948)

³⁸⁴ J. N. McGovern, K. J. Brown and W. A. Kraske, *Tappi* 32, No. 10: 440-448 (Oct., 1949)

³⁸⁵ C. C. Heritage and T. C. Duvall, *Southern Pulp & Paper Mfr.* 11, No. 9: 50, 52-54, 56 (Sept. 15, 1948)

³⁸⁶ J. N. McGovern, K. J. Brown and W. A. Kraske, *Tappi* 32, No. 10: 440-448 (Oct., 1949)

³⁸⁷ J. N. McGovern, K. J. Brown and W. A. Kraske, *Tappi* 32, No. 10: 440-448 (Oct., 1949)

³⁸⁸ J. N. McGovern, K. J. Brown and W. A. Kraske, *Tappi* 32, No. 10: 440-448 (Oct., 1949)

³⁸⁹ S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.* 22, No. 3: 264-274 (Mar., 1930)

TABLE XX

EFFECT OF COOKING TIME ON ASPEN PULP WHEN COOKED IN WATER AT 170° C.

Nominal cooking time, min.	Pulp yield, %	Schopper- Reigler freeness, ml.	Bursting strength, pts./lb. (25 × 40–500)	Tearing strength, g./lb. (25 × 40–500)
0	88.0	570	0.34	0.62
7	86.4	660	0.32	0.75
10	80.6	725	0.30	0.73
15	80.2	630	0.33	0.70
30	77.9	635	0.31	0.67
45	75.0	540	0.24	0.53
60	73.9	520	0.21	0.37

pressure (25° C.) with sodium hydroxide (24 g./l.) followed by mechanical defiberizing is said to produce a superior pulp from aspen in yield of about 90%.³⁹⁰ Chemical consumption is about 5.5% sodium hydroxide.

Whole Wood Fiber from Steam-Treated Wood by Continuous Process (Asplund Process)

The Asplund process, which was developed by a Swedish engineer, Arne Asplund, about 1932, is a continuous pulping process by which green, moist wood chips (45–60% moisture) are defibrated at high temperatures (160–180° C.) in the presence of steam. Steam is used to cause a softening or melting of the middle lamella holding the fibers together so that the wood can be readily separated into fibers.

The Asplund process uses a special piece of equipment, called the defibrator, which was designed for the continuous introduction of chips into a steam chamber, the continuous refining of the chips in the presence of steam, and the continuous discharge of defibrated fibers. The defibrator consists of a feeding arrangement, preheaters, attrition chamber, and a discharge mechanism. Wood chips are fed automatically from a hopper into a horizontal screen and plunger feed which forces the chips into the preheater in the form of a dense "plug" which seals off the steam from the preheater. From the preheater, the chips are carried by means of a screw conveyor into a special refiner equipped with two disks, one of which is stationary and the other of which rotates at 500 to 600 r.p.m. The chips are carried to the center of the stationary disk where they enter the space between the two disks and are worked between the two disks, and finally thrown out to the periphery. For ordinary refining, the disks are about 0.002 in. apart in the grinding zone.

Pressure, temperature, and time of steaming are critical factors which affect the yield and character of the fiber. The treatment should be suffi-

³⁹⁰ K. J. Brown and J. N. McGovern, *Tappi* 33, No. 8: 364–368 (Aug., 1950)

cient to soften the middle lamella and permit easy separation of the fiber, but not so great that the softened chips foul the refiner. Excess heating is to be avoided, since it causes darkening of the pulp and a reduction in yield, due to water-soluble and gas loss. From the standpoint of fiber yield, high temperature and short exposure time is best.³⁹¹

The pressure of the steam used in the preheater and defibrating chamber varies from 90 to 175 p.s.i. Saturated steam is generally used to prevent drying out, since the moisture content of the chips at the time of refining must be 30% or more to prevent charring. The chips are pushed through the preheater in about 50 to 75 seconds, which is sufficient to raise the temperature of the chips to the steam temperature. For jack pine chips $\frac{3}{4}$ in. in length, a steam pressure of 150 p.s.i. for 60 seconds is sufficient.³⁹¹

The fibers obtained by the Asplund process are relatively intact, but the pulp is rather coarse and there are generally some bundles of unseparated fibers up to about 20 mm. in length. The intercellular lignin remains in the fiber walls, which provides stiffness and compressive resistance to the fibers. The yield varies from 92 to 96%. The pH of the stock is about 4.5 to 5.5 or lower, depending upon the species. Usually the pulp is washed before making into walboard or hardboard. In some cases, the pulp is used without washing, in which case it should be neutralized to prevent further hydrolysis. Too high a content of soluble carbohydrates leads to caramelization during hot pressing. Asphalt may be added to the wood chips in a reaction chamber (B-K chamber) where it is intimately mixed with the chips and later distributed uniformly over the surfaces of the fibers by the action of the disk refiner.³⁹² Fire-retarding chemical may be added later.

Pine, spruce, hemlock, aspen, maple, oak, Douglas fir, veneer waste, straw, and bagasse are some of the raw materials which have been used in the Asplund process. Steam consumption averages 1,200 to 1,600 lb. per ton of moisture-free pulp and power consumption varies from 160 to 200 kw.-hr./ton.³⁹³ Power consumption for defibration decreases as a straight-line function in the range of temperatures from 100 to about 160 or 170° C., at which point there is a sharp drop in power consumption.

The Pandia fibrillator can be used to treat wood with steam in a continuous process similar to the Asplund defibrator. This piece of equipment is, however, sold separate from the attrition mill and can therefore be used with any refiner. The operation differs from the Asplund process in that milling is not conducted under elevated steam pressure. Wood waste in the form of slabs, edgings, or round wood can be used.

³⁹¹ C. C. Heritage and T. C. Duvall, *Southern Pulp & Paper Mfr.* 11, No. 9: 50, 52-54, 56 (Sept. 15, 1948)

³⁹² C. C. Heritage and T. C. Duvall, *Southern Pulp & Paper Mfr.* 11, No. 9: 50, 52-54, 56 (Sept. 15, 1948)

³⁹³ V. Longren, *Paper Trade J.* 113, No. 11: 119-122 (Sept. 11, 1941)

Whole Wood Fiber by the Explosion (Masonite) Process

The Masonite process is a patented process in which wood chips about $\frac{3}{4}$ in. long are fed into a battery of digesters or "guns" where they are steamed at high pressure and then exploded. Steam is added to build up a pressure of about 650 p.s.i., which is held for about 30 seconds. Then, this steam is cut off and high-pressure steam is admitted which quickly brings the pressure up to about 1,100 to 1,200 p.s.i. After holding at this pressure for a matter of about 5 seconds, the digester is blown by means of a quick opening valve to release the contents into a cyclone. The explosive effect of this rapid release breaks up the wood chips into a fibrous mass.

The high temperature resulting from steaming causes acid hydrolysis which solubilizes part of the hemicelluloses and softens the lignin. As a result of this hydrolysis, the liquid in the pulp fibers contains a high percentage of sugars and organic acids which must be washed out of the pulp in order to obtain a satisfactory product. Recently, there has been considerable interest in the recovery of useful by-products from the wash liquor. A hemicellulosic by-product having approximately the following analysis is obtained: reducing sugars after hydrolysis for 4 hours in 2% H_2SO_4 , 72%; lignin, 10%; uronic anhydride, 5%; tannin-like materials, 3%; ash, 1.5%; acetyl plus formyl groups, 3%. The sugars are 46% hexose and 26% pentose. The hemicellulose extractables are sold in two forms, a 55% concentrate known as Masonex and a spray-dried product known as Masonoid.

The pulp is fairly acid on coming from the "guns," but it is washed until it is nearly neutral. The fibers are dark in color and are not bleached. They are exceedingly stiff and are not used to any extent in papermaking. However, after refining at a consistency of about 3%, the fibers can be formed into a lightweight, low-density board $\frac{3}{4}$ to 2 in. in thickness suitable for insulating purposes. The wet board is cut into 16-ft. lengths by a knife which travels forward at the same speed as the board as it travels across the sheet.

Masonite fibers contain nearly all the lignin originally present in the wood. The greater part of this lignin has been freed from its carbohydrate bond and is in a highly reactive state. Because of the reactive nature of the lignin, Masonite fibers can be pressed into a product of extreme durability and hardness, known as Masonite Presdwood. This board has a specific gravity of about 1.00.

In making Masonite Presdwood, 16-ft. lengths of board are run into a multiple-opening hydraulic press. A wire screen separates the under side of the board from the bottom platen to permit the escape of steam, but the top side of the board comes into direct contact with the steam-heated,

chrome-finished platen. The amount of pressure and the time of pressing are determined by the thickness and density required in the final board. This may amount to a pressure of over 2,000 tons for each 4- by 16-ft. panel for the highest density board, with drying pressure varying from 85 to 400 p.s.i.³⁹⁴ The final board is very smooth on the top side, but has pronounced wire marks on the bottom side, owing to the wire screen used in pressing. The pressed board may be tempered by treating with oils and baking at high temperature to increase the strength, density, and moisture resistance.

SEMICHEMICAL PULPING

Semichemical pulping is a multistage process involving chemical treatment of wood chips to obtain a softening and partial removal of the ligno-cellulose bonding material, followed by mechanical refining to complete the fiber separation. When originally developed by the United States Forest Products Laboratory in 1926, the semichemical process was described as a three-stage process consisting of (1) a pressure impregnation of wood chips with cooking liquor, (2) a mild digestion with chemicals which are practically neutral and which are capable of maintaining neutrality during cooking, and (3) a mechanical reduction of the softened chips to the fibrous state.^{395, 396} Semichemical pulps are intermediate in yield and properties between groundwood and whole wood fiber on one hand and the full chemical pulps on the other. They cover the yield range of 65 to 85%. The term "semichemical" is not an accurately descriptive name for the process, since the process is, generally speaking, more mechanical than chemical.

The idea of semichemical pulping is old, but impetus has been given to the process in recent years because of decreasing wood resources and increasing wood costs. The development of more efficient refining equipment to replace the older hammer mills, jordans, Clafin refiner, and rod mills has made the process more practical. Semichemical pulping is economical because of the high yields attainable, and the low chemical consumption. Yields are generally about 10 to 40 % higher than conventional pulping processes because only about 25 to 50% of the lignin and 30 to 40% of the hemicelluloses in the wood are removed, compared with a removal of about 90 to 98% of the lignin and about 60 to 80% of the hemicelluloses in ordinary chemical pulping. Because the action of the cooking liquor is directed selectively upon the lignin, it is possible to produce bleached hardwood pulps in a yield of 60% and unbleached pulps in the range of 75 to 80%, compared with a yield of 45 to 50% for chemical pulps. At the same time,

³⁹⁴ *Pulp Paper Mag. Canada* 50, No. 5:79-81 (Apr., 1949)

³⁹⁵ J. D. Rue, S. D. Wells, F. G. Rawling and J. A. Staidl, *Paper Trade J.* 83, No. 13: 106-109 (Sept. 23, 1926)

³⁹⁶ Public Patents, U. S. 1,859,845, 1,859,846, 1,859,847 (May 24, 1932)

a much stronger pulp is produced, on account of the reduced attack on the carbohydrates. One of the advantages of semichemical pulping is its particular applicability to the hardwood species.

Chemicals Used in Semichemical Pulping

Any of the common pulping reagents can be used in the semichemical process. The chemicals which have been suggested are acid sulfite, neutral sodium sulfite, sodium hydroxide, sodium hydroxide plus sodium sulfide, sodium bisulfite, and many others. Acid cooking liquors produce weaker pulps than either neutral or alkaline cooking liquors, strength tending to fall off rapidly at yields over 60%. Alkaline cooking liquors have the disadvantage of producing dark-colored pulps and are not as effective as neutral sulfite or acid sulfite in removing lignin.³⁹⁷ However, coarse, high-yield grades of pulp suitable for corrugating can be produced from hardwoods by a mild treatment with sodium hydroxide, followed by mechanical defiberization.³⁹⁸

The most satisfactory agent for semichemical pulping is a solution of sodium sulfite containing sufficient buffering agent to neutralize the organic acids which are formed when the wood is heated to 120° C. or more.³⁹⁹ Buffering agent is necessary to prevent corrosion of iron equipment, to increase the yield of pulp, and to reduce the cooking time.^{399, 400} Among the buffering agents which have been used are sodium hydroxide, sodium carbonate, sodium sulfide, and sodium sulfate, but the most satisfactory and most widely used agent is sodium bicarbonate. Sodium bicarbonate does not result in as fast pulping as sodium hydroxide, but the color of the pulp is better and the bleach requirement is much lower. The particular advantage of sodium bicarbonate lies in its strong buffering action.

The composition of the liquor, which is known as neutral sulfite semichemical liquor, depends somewhat upon the species and the type of pulp desired. Phelps⁴⁰¹ suggests a ratio of sodium sulfite to sodium bicarbonate of 4 to 1 when making bleachable pulps (70% yield) and a ratio of 7 to 1 when making unbleachable or coarse pulps (80% yield). The whitest pulps are obtained when the pH of the charge at the end of the cooking period is around 7.2 to 7.5.⁴⁰²

Neutral sulfite semichemical liquor can be made by reacting sulfur

³⁹⁷ G. H. Chidester, *Paper Trade J.* 129, No. 21: 452-456 (Nov. 17, 1949)

³⁹⁸ K. J. Brown and J. N. McGovern. Paper given at 35th Annual Meeting of TAPPI, Feb. 20-23, 1950, New York, N. Y.

³⁹⁹ E. L. Keller and J. N. McGovern, *Tappi* 32, No. 9: 400-405 (Sept., 1949)

⁴⁰⁰ M. W. Bray and P. R. Eastwood, *Paper Trade J.* 90, No. 25: 57-60 (June 19, 1930)

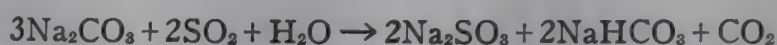
⁴⁰¹ M. W. Phelps, *Northeastern Wood Utilization Council Bull.* 14: 59-70 (Jan., 1947)

⁴⁰² E. L. Keller and J. N. McGovern, *Tappi* 32, No. 9: 400-405 (Sept., 1946)

dioxide with sodium carbonate until the *pH* is lowered to 8.5 to 9.0. When sulfur dioxide is passed into a solution of sodium carbonate, the following reaction takes place:



If the sodium carbonate solution is passed through a packed tower in which sulfur dioxide is rising and the resulting solution (at a *pH* of 4.0) is added to the original solution until a *pH* of 8.0 to 8.5 is obtained, the following reaction occurs:⁴⁰³



In commercial operation, the sulfur dioxide is generally blown into the bottom of an absorption tower while sodium carbonate solution enters at the top and the liquor is recirculated through the tower and tank until the required ratio of sodium sulfite to sodium bicarbonate is obtained. The reaction is generally carried out at high temperature (180° F.) to prevent monosulfite from crystallizing out.

Batch Digestion in Semichemical Pulping

The digestion of wood for semichemical pulping is generally done in a batch process. Rotary digesters are best adapted to the process, although stationary digesters formerly used for sulfite pulping are sometimes employed. The wood is chipped and fed to the digesters, along with the required amount of chemical. After digestion, the cooked chips are dropped into a "hot" chip bin and from there are conveyed to a chip regulator feeding the disk mills where the chips are broken down and defibered. If more than one refiner is used, screening is desirable to remove knots and untreated chips before the final or secondary refining.

In some cases, the chips are refined in the presence of hot cooking liquor, called hot brown stock refining. This aids liquor recovery, since the spent liquor is more efficiently removed from the defibered pulp than from the coarse chips. In other cases, the chips are washed before refining, hot water being applied either at the cooker or at the hot chip bin. Refining while hot reduces power consumption. Magnetic devices are used to remove tramp iron from the chips prior to refining.

Disk refiners (e.g., Bauer, Sprout-Waldron, and Sutherland) are generally used for refining. A single pass through one disk mill may be sufficient in some cases, but ordinarily the stock is passed through two or more refiners. In the first refiner, the disks are set far apart (e.g., 0.010 to 0.012 in.) to break up the chips without excessive power consumption and excessive hydration of the fibers. After being reduced in size in the first

⁴⁰³ F. B. Schelhorn, *Paper Trade J.* 119, No. 23: 223-230 (Dec. 7, 1944)

mill, the pulp is sent to a secondary refiner where the plates are of different shape and are set much closer together than in the first mill. Here, the stock is reduced in freeness and "hydrated" to the desired degree. The consistency is about 4 to 8% during refining.

An interesting new gyratory machine, known as the Curlator (see Chapter VI, "Fiber Preparation") has shown possibilities for the refining of semichemical pulps. The production of these machines is rather low, but the machine will remove shives too small to be removed by screening without producing an undesirable amount of hydration.

Variables in Semichemical Pulping

In semichemical pulping, the ratio of chemical to wood and the time and temperature of cooking are regulated so that there is only a small loss in wood weight. The amount of chemical present at the time of cooking can be established (1) by impregnating the chips and draining off the excess liquor or (2) by adding a definite amount of liquor of known strength. If the first or impregnating method is used, the impregnating liquor can be reused indefinitely when making coarse pulps and can even be reused many times when making bleachable grades. If the second method is used, a weak liquor equivalent to about one-half the normal amount of chemical and one-half the normal concentration may be added,⁴⁰⁴ in which case the cook is carried to exhaustion of the chemical;^{405, 406} or a relatively strong liquor may be used and the cook may be stopped before pulping is complete and the chemical returned for reuse.

Penetration of the chips with liquor is very important in semichemical pulping in order to obtain a uniform pulp having a minimum of fiber bundles. Small chip size aids penetration, but a more important factor is the ability of the chips to hold a large amount of liquor, which depends upon the density of the wood. Low-density hardwoods (e.g., aspen) retain sufficient chemical after impregnation to pulp readily. High-density hardwoods (e.g., birch) do not retain sufficient chemical on impregnation to produce a bleachable pulp, and hence satisfactory pulping with these species is dependent upon diffusion of spent chemicals out of chips and replacement of this spent liquor with fresh chemical.⁴⁰⁷ Penetration of liquor into the wood chips can be facilitated by the use of hydrostatic pressure.

The effect of time and temperature in semichemical pulping is similar to the effects obtained in alkaline pulping, except that the neutral liquor

⁴⁰⁴ M. W. Bray, *Paper Trade J.* 120, No. 21:212-214 (May 24, 1945)

⁴⁰⁵ M. W. Bray, *Paper Trade J.* 120, No. 21:212-214 (May 24, 1945)

⁴⁰⁶ M. W. Bray and J. S. Martin, *Paper Trade J.* 120, No. 3:25-28 (Jan. 18, 1945)

⁴⁰⁷ Fiber Containers, Report on Conference on Semichemical Pulping, 66-74 (Nov., 1949)

reduces the wood to pulp more slowly than sodium hydroxide.^{408, 409} Increasing the temperature of digestion 10° C. approximately doubles the rate of pulping over the range of 140 to 170° C.⁴¹⁰ The cooking liquor is relatively specific for lignin, and it has been claimed that no substances other than lignin are removed up to temperatures of 170° C. in the pulping of aspen.⁴¹¹

The conditions of semichemical pulping vary according to whether high-grade pulp or coarse-grade pulp is desired.⁴¹² When making coarse grades of pulp, the digester is charged with unbarked wood and the proper amount of cooking liquor, heated to temperature in 1 hour and held there 1 to 3 hours. The presence of bark lowers the density and strength of the pulp somewhat, but moderate amounts do not require any significant changes in cooking conditions.⁴¹³ Pulp suitable for corrugated board is made commercially by pulping a mixture of unbarked hardwoods with a small percentage of softwoods in neutral sulfite liquor, using a chemical ratio of 7 to 1, 13% chemical on the wood, a cooking time of about 4½ hours, and a pressure of 100 to 120 p.s.i.^{414, 415} The cooked chips are then refined without washing in a disk refiner. The consistency of the chips entering the refiners is about 42%, but hot shower water reduces the consistency of the chips at the plate to about 10% and the consistency of the stock leaving the refiners to about 3.5%.⁴¹⁶ The yield of pulp is 80 to 90% of the weight of the original wood (on a bark-free basis). A process suitable for the manufacture of corrugated paperboard from southern New England hardwood has been described by Aries.⁴¹⁷ The conditions are as follows: chemical ratio of sodium sulfite to sodium bicarbonate of 5 to 1; concentration of liquor (calculated as sodium carbonate) of 35 g./l.; amount of chemical on the basis of the wood, 14%. The charge was cooked at a temperature of about 170° C. and a pressure of about 100 p.s.i., and the cook was held at maximum temperature for 2 to 3 hours. Yields of about 70% were obtained, which is low for this type of pulp.

⁴⁰⁸ M. W. Bray and P. R. Eastwood, *Paper Trade J.* 93, No. 17: 188-192 (Oct. 22, 1931)

⁴⁰⁹ M. W. Bray and P. R. Eastwood, *Paper Trade J.* 90, No. 25: 57-60 (June 19, 1930)

⁴¹⁰ M. W. Bray and P. R. Eastwood, *Paper Trade J.* 93, No. 17: 188-192 (Oct. 22, 1931)

⁴¹¹ F. G. Rawling and J. A. Staidl, *Paper Trade J.* 81, No. 8: 49-51 (Aug. 20, 1925)

⁴¹² H. J. Perry, *Paper Ind.* 31, No. 2: 210-213 (May, 1949)

⁴¹³ E. L. Keller. Paper given at 35th Annual Meeting of TAPPI, New York, N. Y. (Feb. 20-23, 1950)

⁴¹⁴ J. C. W. Evans, *Pulp Paper Mag. Canada* 50, No. 9: 65-69 (Aug., 1949)

⁴¹⁵ J. C. C. Gain, *Pulp Paper Mag. Canada* 51, No. 3: 211-213, 217 Convention Issue (1950)

⁴¹⁶ J. C. C. Gain, *Pulp Paper Mag. Canada* 51, No. 3: 211-213, 217, Convention Issue (1950)

⁴¹⁷ R. S. Aries, *Paper Trade J.* 128, No. 2: 13-18 (Jan. 13, 1949)

Bleachable grades of semichemical pulp are made by cooking barked wood using a higher chemical ratio, lower temperature and pressure, and a longer cooking schedule. The original semichemical process described by the United States Forest Products Laboratory involved: (1) steaming of the wood chips for $\frac{1}{2}$ hour at atmospheric pressure, (2) introduction of liquor and application of pressure of 100 p.s.i. at a temperature of 120 to 125° C. for 1 hour, (3) removal of excess liquor not absorbed by chips by blowing back to the liquor tank for reuse in succeeding cooks, and (4) digestion at 140 to 160° C. for 1 to 6 hours. This process is followed today, except that higher temperatures (up to 170–175° C.) are used.⁴¹⁸ The chemical ratio used for making bleachable grades of semichemical pulp is generally about 4 to 1, the total chemical absorbed about 17–18%, and the total cooking time between 5 and 8 hours. The yield obtained from poplar by this process is generally about 68 to 70% and the pulp may be semi-bleached after defibering in a refiner to a brightness of 70 using single stage hypochlorite. The shrinkage of the pulp on bleaching is less than 5% of the unbleached pulp.

Continuous Digestion in Semichemical Pulping

Continuous cooking equipment has been used for semichemical pulping. It has the advantage of continuous operation and of furnishing chips to the refiner at higher temperature. A special piece of equipment suitable for continuous semichemical pulping is the defibrator-chemipulper. This is similar to the Asplund defibrator, except that a reaction chamber is used between the feed and defibrator to increase the time the chips are subjected to heat. The reaction chamber consists of a series of closed, horizontal, stainless steel screws. The chips enter the middle of the top screws and are split and conveyed in two portions toward the ends where they are carried to the center and passed on to the next set of screws.

The defibrator-chemipulper embodies a combination of continuous digestion and continuous refining under pressure. When used for semichemical pulping, the controlled addition of chemicals can be made at the reaction chamber to accelerate the softening action. The use of chemical reduces the power consumption about 40% and increases the production about 50% over the regular Asplund defibrator.⁴¹⁹ The chemical is blown in with the steam at temperatures up to 180° C. The speed and pitch of the screw determines the period of retention of the chips in the reaction chamber. The period of retention is generally about 10 to 12 minutes when coarse, corrugating pulps are made. Yields are in the neighborhood of 75 to 85%, depending upon the amount of chemical used and the period of re-

⁴¹⁸ H. J. Perry, *Paper Ind.* 31, No. 2: 210–213 (May, 1949)

⁴¹⁹ *Tech. Assoc. Papers* 25, 97–98 (June, 1942)

tention in the reaction chamber. Commercial pulps can be made in yields of about 85 to 87% by treating with 2 to 3% sodium hydroxide on the weight of the wood and a retention time of 4 to 5 minutes.

Recovery of Chemical in Semichemical Pulping

The recovery of chemical from semichemical pulping liquor has become an important problem as this type of pulping has increased. The seriousness of the situation depends upon the type of process used and the location of the mill. There is no particular problem in the reuse of impregnating liquors in those mills practicing a two-stage process involving impregnation and liquor withdrawal, since the impregnating liquor can be reused over again after the lost chemical has been replenished. The reuse of spent liquor presents more of a problem, but chemical and heat recovery is customarily practiced in mills making coarse papers (where very little dissolved matter is removed from the wood) by using up to 50 to 100% of spent liquor in each cook. Keller and McGovern^{419a} found that the reuse of neutral sulfite semichemical spent liquor from aspen had no effect on the strength of the pulp, and the yield was increased by about 2% (74 to 76%), although the brightness of the pulp was decreased about 4% (51 to 47%). The liquor reached equilibrium after ten cycles of reuse. However, many semichemical plants are forced to dump a large part of their black liquor to the sewer which is undesirable from the standpoints of increased chemical cost and stream pollution.

Burning of evaporated spent liquor is not a satisfactory solution to the problem of chemical recovery, since salts, in addition to sodium sulfite, are obtained. These salts cannot be sulfited without the formation of thiosulfates, hydrogen sulfide, and free sulfur. Burning under controlled conditions is said to produce sodium sulfite directly without producing too much sulfate, but a satisfactory process has not been fully perfected. Another proposed recovery process is based upon burning the evaporated liquor to produce sodium sulfide, which is then oxidized to sodium sulfite under controlled conditions. If the semichemical operation is carried out jointly with a sulfate mill, satisfactory reuse of the liquor can be made by disposing of it in the recovery system of the sulfate mill, thus utilizing the recovered chemicals in the preparation of the sulfate cooking liquor. The potential heat to be recovered from the burning of semichemical spent liquor is less than that from conventional soda and sulfate spent liquors because of the lower heat value of the solids and the lower concentration of solids in the liquor to the evaporator.

^{419a} E. L. Keller and J. N. McGovern. Paper Presented at 36th Annual Meeting of TAPPI, New York, N. Y. (Feb. 19-22, 1951)

Properties of Semichemical Pulps

Semichemical pulping is well suited to the hardwood species. It is not so well suited to the softwood species. One disadvantage of softwoods is their high chemical requirement; for example, McGovern and Keller⁴²⁰ found that the pulping of jack pine by the neutral sulfite process required about 45% more chemical (on a sodium oxide basis) than pulping by the sulfate process. Furthermore, softwood semichemical pulps have a high lignin content and comparatively low strength, compared with softwood pulps produced by other pulping processes.

Hardwood semichemical pulps are stronger than hardwood sulfite pulps and about equal or slightly higher in strength than hardwood sulfate pulps.⁴²¹ This is shown in Table XXI, where aspen semichemical pulp is compared for strength with aspen pulp produced by the full chemical process (sulfate, soda, and sulfate processes).⁴²² On the same basis of compari-

TABLE XXI

COMPARATIVE STRENGTHS OF ASPEN PULPS PRODUCED BY DIFFERENT PULPING PROCESSES

	Burst	Tear
Neutral semichemical, bleached	110	105
Neutral semichemical, unbleached	80	85
Sulfate, unbleached	90	75
Sulfate, bleached	80	90
Soda, unbleached	65	75
Soda, bleached	50	60
Sulfite, unbleached	50	60

son, unbleached spruce sulfite would have a burst of 100, or slightly less than the aspen neutral semichemical bleached pulp. In the yield range between 70 to 80, Chidester reports⁴²³ bursting strengths of 0.80 and 0.90 point per pound per ream (25 × 40–500) for birch, aspen, and cottonwood, which are about 75 to 80% of the corresponding values for spruce sulfite. When compared at low freeness values, the tearing strength of hardwood semichemical pulp is equal or slightly better than the tearing strength of semichemical softwood pulp.⁴²⁴

It is possible to group the various hardwood species into fairly well-defined categories, depending upon the properties of the pulp which they

⁴²⁰ J. N. McGovern and E. L. Keller, *Pulp Paper Mag. Canada* 49, No. 9: 93–100 (Aug., 1948)

⁴²¹ G. H. Chidester, *Paper Trade J.* 129, No. 21: 451–456 (Nov. 17, 1944)

⁴²² E. R. Schafer, Forest Prod. Lab., *Lake States Aspen Report* No. 14 (Oct., 1947)

⁴²³ G. H. Chidester, *Paper Trade J.* 129, No. 21: 451–456 (Nov. 17, 1949)

⁴²⁴ G. H. Chidester and J. N. McGovern, *Paper Trade J.* 108, No. 6: 57–58 (Feb. 9, 1939)

produce.⁴²⁵ In general, both the low-density, low-lignin content hardwoods (e.g., aspen) and the high-density, intermediate-lignin content hardwoods (e.g., birch) produce pulps of high strength, whereas the high-density, high-lignin content hardwoods (e.g., oak) produce pulps of low strength and high lignin content. The most widely used species in the northern states are aspen, birch, beech, and maple. Of these aspen and birch produce pulps of particularly good color and strength. In the southern states, the species commonly used are the gums, tupelos, extracted chestnut, and oak. The color of the pulp is fair when light-colored woods (e.g., birch, poplar, maple, and gum) are used, being close to the color of unbleached sulfite under optimum pulping conditions.

There is a growing tendency to use hardwoods for semichemical pulping in the same proportion as they occur naturally in mixed stands. In spite of the differences in species, no serious trouble in pulping mixtures has arisen, although there is a difference in the color and strength of the pulp produced.

Papers produced from semichemical hardwood pulps are characterized by low wet strength, but the dry strength is generally quite high. The strength of the pulp increases with decreasing yield, strength being very low at yields over 80%.⁴²⁶ In the case of coarse pulps used for making corrugating medium, coarse wrapping paper, linerboard, hardboard, insulating board, and roofing felt, the most desirable combination of high yield and acceptable strength is obtained in the yield range of 70 to 80%. Such high yield pulps are coarse and shivy unless heavily refined, but it is possible to produce semichemical pulps in yields as high as 75% having fibers which are well separated.⁴²⁷

Pulps for the finer grades of paper (e.g., book, bond, glassine, waxing, and tissue) are produced in lower yield. Bleachable grades are made by cooking to a lignin content of about 10%. Such a low yield semichemical pulp can be bleached in a single-stage treatment with hypochlorite or peroxide to a brightness level of 70 to 75% without appreciable loss in yield. Multistage bleaching with chlorine, caustic extraction, and hypochlorite reduces the yield, but appreciably increases the strength, and raises the brightness level to 80% or more. Optimum bursting strength is obtained at a yield between 50 to 60%.⁴²⁸ Ritter and coworkers⁴²⁹ obtained an exceptionally high-strength semichemical pulp from Douglas fir in yield of 57%

⁴²⁵ *Fiber Containers* "Report on Conference on Semichemical Pulping," pp. 66-74 (Nov., 1949)

⁴²⁶ G. H. Chidester, *Paper Trade J.* 129, No. 21: 450-456 (Nov. 17, 1949)

⁴²⁷ G. H. Chidester, *Paper Trade J.* 129, No. 21: 451-456 (Nov. 17, 1949)

⁴²⁸ G. H. Chidester, *Paper Trade J.* 129, No. 21: 451-456 (Nov. 17, 1949)

⁴²⁹ H. E. Peterson, M. W. Bray and G. J. Ritter, *Paper Trade J.* 121, No. 2: 13-18 (July 12, 1945)

by treating the pulp with chlorine and extracting with alkali to remove the residual lignin.

When used alone in the furnish, semichemical pulps produce papers having a high bursting strength, but the paper tends to be stiff and rattly and low in tearing and folding strengths, on account of the rapid hydrating properties of the pulp. When properly prepared and mixed with other pulps, it is possible to use a fairly high percentage of semichemical pulp in book papers without detracting seriously from the opacity of the paper.

MISCELLANEOUS PULPING PROCESSES FOR WOOD

In addition to the regular commercial pulping agents, many other chemicals can be used for pulping wood. Most of these chemicals have certain disadvantages, such as high cost, poor yields, or inferior pulp, and consequently are not widely used. However, a few processes are of sufficient interest to be mentioned.

Pulping with Sodium Sulfite

Sodium sulfite was among the earliest chemicals suggested for pulping, having been described by Cross in 1830. At first, sodium sulfite was tried mostly for the pulping of straw, bagasse, and cornstalks, but later was used for the pulping of wood.

Sodium sulfite is well suited to semichemical pulping, as pointed out in a previous section, but it is not well suited to the full chemical pulping of wood. Two disadvantages of neutral sodium sulfite as a pulping agent are the high temperature and high percentage of chemical which are required. The minimum practical cooking temperature is 180°C ., which is about 10° higher than that required in the sulfate process. To obtain satisfactory pulping, about 45 to 55% chemical on the wood weight is required, which is about 50% more chemical (on a soda basis) than that required in the sulfate process. The color of the pulp is, however, much better than that obtained with the sulfate process. The bright color of the pulp produced was a decided advantage of this process until a satisfactory method of bleaching sulfate pulps was discovered, after which this advantage became of secondary interest. Pulps produced with sodium sulfite have high strengths in comparison with wood cooked by the conventional processes, especially in the case of hardwoods. Sodium sulfite is a milder cooking agent than sodium hydroxide and has less harmful effect on the yield when used in excess.

The monosulfite process would probably find more widespread application if it were not for the high chemical demand and lack of an effective recovery system. Because of the high chemical demand, recovery is an economic necessity, but unfortunately there is no simple straightforward

method of chemical recovery. If waste liquor from the monosulfite process is smelted, a considerable amount of sodium sulfide (generally over 40%) is formed, together with sodium carbonate. When this recovered liquor is treated with sulfur dioxide, the sulfide in the liquor is converted into thiosulfate, which has a deleterious effect on the bleachability of the pulp.⁴³⁰ The smelt can be used as make-up for the kraft process, but this necessitates locating the mill in conjunction with a kraft mill.

One of the most significant pulping processes utilizing sodium sulfite is the Keebra process,⁴³¹ which utilizes, in addition to sodium monosulfite, other sodium salts such as bisulfite, sulfate, thiosulfate, hydroxide, carbonate, and bicarbonate. Substitution of sodium bicarbonate for part of the sodium sulfite increases the rate of pulping, decreases the consumption of chemical, reduces the attack on the cellulose, and reduces corrosion.⁴³² At one time, the Keebra process was used in several places, but its use was gradually discontinued, principally because of the difficulties in chemical recovery.

Pulping with Nitric Acid

Nitric acid was one of the earliest known pulping agents, but high cost and lack of acid-resistant equipment has prevented its commercial use until recent times. Recently, nitric acid has been used on a small scale in Germany for the cooking of beech, and in the United States and Japan for the cooking of agricultural residues. Nitric acid pulping has the advantages of (1) short cooking time, (2) low cooking temperature, (3) low required acid concentration, and (4) high yields.

Nitric acid is a successful pulping agent, whereas other mineral acids are not, because nitric acid pulping involves nitration and oxidation of the encrusting materials, as well as hydrolysis. Lignin, in particular, is attacked by nitric acid, nitration being the predominant reaction. Concentrated nitric acid cannot be used because of its reaction with the cellulose and other carbohydrates which consume excessive amounts of acid and weaken the fiber.

To obtain a satisfactory pulp from wood, a 5 to 8% solution of nitric acid is used, and 5 parts of this solution used on the basis of the wood weight. The digestion can be carried out at atmospheric pressure and at temperatures from room to 100° C. The time of digestion is very short, ranging from 1 to 3 hours. High yields of pulp can be obtained under these circumstances. The lignin residues are partly soluble in water and partly soluble in dilute alkali. An alkaline extraction of the pulp helps to remove

⁴³⁰ K. A. Kobe and J. M. Hanson, *Paper Trade J.* 171, No. 2: 13-14 (July 8, 1943)

⁴³¹ L. Bradley and E. P. McKeefe, *Paper Trade J.* 88, No. 8: 72-75 (Feb. 21, 1929)

⁴³² M. W. Bray and P. R. Eastwood, *Paper Trade J.* 90, No. 25: 57-60 (June 19, 1930)

soluble by-products. A high percentage of the acid can be recovered for reuse.

Some of the proposed processes for the pulping of wood by nitric acid have been described in a survey by Aronovsky and coworkers, as shown in Table XXII. The nitric acid process used in Germany for the preparation

TABLE XXII

CONDITIONS USED IN NITRIC ACID PULPING OF WOOD

Patentee	Dreyfus	Miles	Solechnik
Type of wood used	Poplar	Poplar	Poplar
Concn. of nitric acid	6%	8%	7%
Time of digestion	3 hours	9 hours	1.5 hours
Temperature of digestion .	80° C.	100° C.	98° C.
Concn. of alkali	2.5% (boiling)	Dilute	0.05–0.25% ^a

^a At 40° C. for 2 hours.

of high alpha cellulose was carried out as follows. Beech chips were impregnated with nitric acid at a concentration of 12 to 15% in the ratio of 3.5 parts of acid per part of dry wood for 3 hours at 40 to 45° C. The liquor was then drawn off, and hot water was added to bring the nitric acid concentration to 4%. This charge was pulped at 70 to 95° C. After cooking, the charge was first washed with 1% and then with 4% sodium hydroxide, and finally with hot water. The pulp was bleached, and in the final stage, purified with 12% sodium hydroxide. The cooked pulp resembles well-cooked, high alpha pulp, but if the pulp is overcooked, it has a high oxycellulose content.

Pulping with Organic Solvents

Most of the work on the pulping of wood with organic solvents has been done on sawdust. The pulp obtained is not suitable for papermaking because of its short fiber, but can be used for chemical purposes. The lignin is isolated by this process with far less degradation than occurs in ordinary pulping, and most of the investigational work has been directed along the line of lignin recovery. So far, the processes have not been used commercially, but are used in the laboratory for the isolation of lignin for study.

Among the organic solvents which have been suggested are alcohols, dioxane, and glycols. Alcohols, in particular, have been widely used.^{433–436}

⁴³³ S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.* 28, No. 11: 1270–1276 (Nov., 1936)

⁴³⁴ A. J. Bailey, *Pacific Pulp Paper Ind.* 14, No. 3: 24–27 (Mar., 1940)

⁴³⁵ H. Erbing, *Papier-Fabr.* 37, No. 20: 168–170 (May 12, 1937)

⁴³⁶ J. M. McMillen, R. A. Gortner, H. Schmitz and A. J. Bailey, *Ind. Eng. Chem.* 30, No. 12: 1407–1409 (Dec., 1938)

In general, the normal primary alcohols are better pulping agents than the secondary or tertiary alcohols, normal butyl and amyl alcohols being best.⁴³⁷ Hardwoods are better suited for pulping in alcohol-water mixtures than softwoods. It is possible to obtain a pulp from aspen equal to soda pulp in strength by cooking in a solution of water and normal butyl alcohol in equal volume ratios for 2 hours at 188° C., using a liquor-to-wood ratio of about 7 to 1.⁴³⁸

Other Pulping Agents

Some of the other agents which have been suggested for the pulping of wood are chlorine, sodium hydrosulfite,⁴³⁹ sodium chlorite,⁴⁴⁰ chlorohydrins, and acetic acid.⁴⁴¹ Chlorine is not used commercially for the pulping of wood, but it is used for straw and other grasses. Sodium thiosulfate is a strong pulping agent, although some chemists regard it as a detriment to pulping. Bray and Singer⁴⁴² found sodium thiosulfate to have a beneficial effect in increasing the rate of pulping and strength of pulp obtained in the soda and sulfate processes. Sodium chlorite offers promise as a pulping agent for wood whereby the lignin may be removed without appreciably affecting the carbohydrate residues. It has been tried in Germany for the pulping of wood,⁴⁴³ but long cooking periods are required.

McKee⁴⁴⁴ describes the use of hydrotropic solutions, i.e., aqueous salt solutions which promote greater solubility than water alone. Some of the materials suggested are the alkali salts of xylenesulfonic, cymenesulfonic and benzoic acids. Lignin is soluble in the neutral salt solution at 30 to 40% concentration, and recovery of chemical is made by diluting the solution to 10%, filtering off the precipitated lignin, and then evaporating the filtrate to the concentration of the original solution.

DEINKING OLD PAPERS

Waste papers furnish an abundant, low-cost source of raw material for making certain grades of paper and paperboard, among which are container board, boxboard, wrapping paper, printing paper, and other grades.

⁴³⁷ S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.* 28, No. 11: 1270-1276 (Nov., 1936)

⁴³⁸ S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.* 28, No. 11: 1270-1276 (Nov., 1936)

⁴³⁹ R. L. Hossfeld, R. A. Gortner and F. H. Kaufert, *Ind. Eng. Chem.* 35, No. 6: 717-720 (June, 1943)

⁴⁴⁰ R. Runkel and P. Schoeller, *Papier-Fabr.* 40, No. 49: 201-202 (Dec. 15, 1942)

⁴⁴¹ W. A. Wiltshire, *Proc. Tech. Sec. Papermakers' Assoc. Gt. Britain Ireland* 24: 347-353 (Dec., 1943)

⁴⁴² M. W. Bray and B. Singer, *Paper Trade J.* 125, No. 8: 81-85 (Aug. 21, 1947)

⁴⁴³ G. P. Vincent and J. F. White, *Paper Ind.* 27, No. 6: 880-881 (Sept., 1945)

⁴⁴⁴ R. H. McKee, *Ind. Eng. Chem.* 38, No. 4: 382-384 (Apr., 1946)

By far the largest amount of waste paper is used in making multi-ply paperboards where the waste paper is used in the inner plys. The pulping process is principally mechanical. Old newspapers, wrapping papers, boxes, and other mixed papers are disintegrated at high temperature in a large beater, called a breaker beater, until the waste paper has been reduced to the desired state of fineness. The defibered stock is then used directly in making paperboard after a small degree of refining.

In order to produce a white pulp from waste papers suitable for book papers, it is necessary to remove the ink from the waste paper. The process of doing this is known as deinking. The deinking process consists of sorting, dusting, defibering, cooking, washing, bleaching, refining, and screening waste paper.⁴⁴⁵⁻⁴⁴⁸ There are two basic steps in deinking: (1) loosening the ink and defibering the stock and (2) washing the ink from the fibers. Deinking has been described as basically a laundry problem. Wetting, detergent action, and dispersion are involved in the suspension and removal of ink, sizing, coating material, and fillers which are present in the waste papers.

Types of Papers Used in Deinking

The waste papers used by the paper industry include a wide range of waste material. This material is collected by waste paper dealers, graded, and sold according to prescribed standards. Originally, there were three recognized grades: (1) shavings and cuttings not printed upon, (2) book stock which was printed, and (3) mixed waste papers. There are now many more grades than this. These differ widely in price, according to the quality of the material, and fluctuate widely in price according to the available supply and demand.

The most desirable papers for deinking are fine shavings and cuttings, ledger stock, and magazine stock. Most waste papers, especially the lower grades of mixed papers, must be sorted to remove undesirable papers such as groundwood papers, carbon papers, waxed papers, impregnated papers, glassine, parchment, bits of cloth, typewriter ribbons, bits of wood and dirt, highly colored covers or posters, and wet strength papers. Dusting of the paper by beating and tumbling is sometimes used to loosen and separate the dust and dirt, but the use of dusters is gradually becoming obsolete.

Purchase specifications for waste paper for deinking generally limit the groundwood content to a maximum of 1 to 4%. Groundwood papers are undesirable because they are difficult to deink and because they turn

⁴⁴⁵ C. A. Shubert, *Paper Trade J.* 93, No. 13: 137-140 (Sept. 24, 1931)

⁴⁴⁶ H. A. Morrison, *Paper Trade J.* 94, No. 18: 239-241 (May 5, 1932)

⁴⁴⁷ H. O. Ware and R. T. Washburn, *Paper Trade J.* 122, No. 26: 283-287 (June 27, 1946)

⁴⁴⁸ J. J. O'Conner, *Tech. Assoc. Papers* 10: 121-122 (June, 1927)

brown during deinking. Excess groundwood in the waste papers results in brown-colored specks in the final pulp. Papers containing groundwood can be identified by the color reaction obtained when the paper is stained with aniline sulfate (yellow), phloroglucinol (red), or a solution of sodium hydroxide (yellow).

Wet strength paper is objectionable because of the resistance of the paper to fiber separation. High temperatures and low pH are required for the disintegration of these papers (see Chap. XII). Glassine and parchment papers are difficult, if not impossible, to defiber. Waxed, resin-impregnated, and resin-coated papers are resistant to water and cannot be defibered by ordinary deinking methods.

Pigment-coated book papers containing starch as the binder are readily deinked, but coated papers containing insolubilized casein as the binder must be heated to a temperature of at least 160° F. at a pH around 9 to 10. Casein-coated papers cause trouble by the casein breaking down into ammonia and carbon dioxide during cooking, thus creating foam. Foam is particularly troublesome when casein is heated in the presence of calcium carbonate, which may be present as a coating pigment.⁴⁴⁹ Further trouble may be caused by the carbon dioxide reacting to form bicarbonates, which lower the pH of the cooking liquor.

Chemicals Used in Deinking

Much deinking is done with plain alkali, but detergents and dispersing agents such as soaps, sulfonated oils, bentonite, sodium metasilicate or silicate penthydrate, and other surface-active substances are sometimes used in combination with alkali. An ideal deinking formula would include an alkali to saponify the varnish or vehicle of the printing ink, a detergent to aid in the wetting of the pigment in the ink, a dispersing agent to prevent agglomeration of the pigment particles after release from the paper, and an absorption agent to bind the pigment and prevent redeposition on the fiber.

Alkali is used in the deinking formula for two purposes: (1) to remove rosin sizing from the paper and (2) to saponify the ink vehicle and release the pigment in the ink. There is generally about $\frac{1}{2}$ to 2% ink on the weight of the paper, and this must be completely removed if white pulp is to be produced. From the standpoint of ease of deinking, there are three principal types of inks: (1) drying, oil-base inks, (2) non-drying, oil-base inks, and (3) inks having a synthetic resin base. Drying, oil-base inks which are slightly oxidized can be readily saponified by alkali. However, completely oxidized oil-base inks, non-drying, oil-base inks, and inks having a synthetic resin base cannot be completely saponified by alkali of ordinary concentration, and consequently special methods of deinking must be used

⁴⁴⁹ A. O. Bragg, *Paper Trade J.* 112, No. 17: 207-214 (Apr. 24, 1941)

for papers containing these inks. Solvents (e.g., tri- or tetrachloroethylene, benzene, or carbon tetrachloride) or soaps and detergents can be used to aid in the deinking of these papers.

Sodium carbonate is the most widely used alkali in deinking, although considerable sodium hydroxide is used. Sodium carbonate is a milder agent than sodium hydroxide and results in less oxidation of the fiber and less fiber loss. When used alone, about 3 to 8% sodium carbonate, or about 2 to 4% sodium hydroxide, is sufficient for the deinking of most papers. For papers which are hard to deink, a mixture of 2½% sodium carbonate and ½% sodium hydroxide works best.⁴⁵⁰ In general, only a small part of the alkali is consumed in the cook. Laboratory results have shown that the consumption of alkali is in the range of about 0.25 to 1.0%, based on the weight of the paper,⁴⁵¹ so that most of the original alkali appears in the waste liquor.

In deinking ordinary rosin-sized papers, the alkali reacts with the rosin to form rosin soap, which acts as a detergent for the ink particles. If unsized papers are used, no rosin soap is formed, and hence special detergents may be required. The development of new wetting agents and detergents within recent years has made available a host of materials which show promise as an aid in removing printing ink, even under conditions of hard water and low pH.

Sodium silicate is sometimes used for all or part of the alkali. The use of silicate produces a whiter, brighter pulp than sodium hydroxide or sodium carbonate because of its high degree of surface activity. Silicate is effective at a lower pH than sodium hydroxide, which is important when deinking groundwood papers. The more alkaline grades of silicate are preferred. A suitable grade is one containing 1 part Na₂O to 1.6 to 1.7 parts SiO₂, or sodium metasilicate (Na₂SiO₃ · 5H₂O). The amount of silicate used depends on the consistency of the pulp; at 20% consistency, 2% sodium metasilicate plus 0.2% rosin soap on the weight of the pulp is sufficient, whereas at 5% consistency, as much as 8 to 9% metasilicate and 0.8% rosin soap may be required.⁴⁵² High-grade waste paper can be deinked by using 3% of 42° Baumé silicate and 1.5% sodium hydroxide at a temperature of 150 to 170° F. for a time of 45 minutes.⁴⁵³

Once the pigment has been released, dispersing and absorptive agents are necessary to prevent the pigment from becoming redeposited on the surface of the fibers, which are strongly adsorptive because of their swollen

⁴⁵⁰ F. C. Clark, *Paper Trade J.* 116, No. 13: 147-149 (Apr. 8, 1943)

⁴⁵¹ H. P. Bailey and A. H. Nadelman, *Paper Trade J.* 125, No. 2: 13-15 (July 10, 1947)

⁴⁵² R. C. Merrill, *Tappi* 32, No. 11: 520-528 (Nov., 1949)

⁴⁵³ R. C. Merrill, *Tappi* 32, No. 11: 520-528 (Nov., 1949)

condition. One patented process calls for a mixture of high-silica sodium silicate and a fatty acid.⁴⁵⁴ The silicate is added first, and after it is thoroughly mixed, the fatty acid is added. This forms a colloidal solution of silicic acid and sodium oleate, which acts as a dispersing agent and prevents redeposition of the pigment particles on the fibers. Bentonite may be used for the same purpose⁴⁵⁵ and to prevent the agglomeration of carbon black particles around curds of calcium or magnesium soaps formed during deinking. Other clays may be used, or the clay may be obtained from the filler in the paper. Waste book and magazine stock has been successfully deinked for years, and part of the ease of deinking these papers can be attributed to the presence of clay fillers. Bragg⁴⁵⁶ points out that 0.75% bentonite completely absorbs the oil and scum in a pulp containing unsaponifiable ink.

Considerable interest has been shown recently in the use of peroxide as an aid to deinking operations. Peroxides are particularly effective in combination with silicate. A suitable formula is 1 to 3% hydrogen peroxide, 3 to 6% silicate (58.5°–1.6 ratio), and 0.5 to 2.0% sodium hydroxide to be applied at a temperature of 120 to 160° F. over a period of 35 to 90 minutes.^{457, 458} If sodium peroxide is used in place of hydrogen peroxide, no sodium hydroxide need be added. When used conjointly with alkaline liquors, peroxide results in better fiber separation and, in many cases, higher washed pulped brightness than is possible with alkali alone. The advantages of peroxide are becoming of great interest as the manufacturer of deinked papers is faced with more and more groundwood in his raw material supply. Regular alkaline liquors have a detrimental effect on the brightness of pulps containing groundwood, but peroxide helps to prevent darkening and even results in a simultaneous bleaching beyond and above this point. Furthermore the presence of peroxide in the deinking formula helps to prevent color reversion of the pulp.

Mechanical Treatment Used in Deinking

There are no standard conditions for deinking, and widely different practices are followed in different mills. In general, there are three different methods: (1) disintegration of the stock in a beater or pulper, followed by cooking in cookers; (2) disintegration of the stock in a beater or pulper, followed by cooking in the same pulper; or (3) cooking of the stock in a cooker without previous disintegration. Either high (20–35%) or low (4–10%) density disintegration is used.

⁴⁵⁴ F. H. Snyder and S. F. M. Maclaren, *Paper Trade J.* 98, No. 17: 216–218 (Apr. 26, 1934)

⁴⁵⁵ S. D. Wells, *Paper Mill News* 67, No. 20: 12–24 (May 13, 1944)

⁴⁵⁶ A. O. Bragg, *Paper Trade J.* 112, No. 17: 207–214 (Apr. 24, 1941)

⁴⁵⁷ R. C. Merrill, *Tappi* 32, No. 11: 520–528 (Nov., 1949)

⁴⁵⁸ E. W. Turley, *Paper Ind.* 31, No. 3: 340 (June, 1949)

Most deinking mills use the first method described above, namely, low density disintegration, followed by cooking. An illustration of this method would be as follows. The stock is broken up in a breaker beater or special pulper at a consistency of 4 to 9%, after which the pulp is cooked in a stationary circulating type cooker or in a rotary cooker at a temperature of 160 to 210° F. for 1 to 5 hours. In some cases, higher consistency disintegration may be used. It has been shown that about 77% of the deinking and defibering takes place in the initial pulping and only about 21% during cooking.⁴⁵⁹

In the second method, the stock is disintegrated and cooked in the pulper, which may be a large beater, hydropulper, or a tank and pumping system. The power required is used for circulation and defibering; there is no actual "beating" of the stock in the sense of "hydrating" the fiber. Pulping consistencies vary from 7 to 25%. High-consistency pulping speeds up defibering, reduces the amount of chemical required, and results in pulp of higher freeness, compared with low-consistency pulping. The temperature range is usually 140 to 180° F., and the cooking time is usually 2 to 5 hours. There is no recovery of cooking liquor in this method. Typical formulas and procedures used in this method of deinking are given in Table XXIII.⁴⁶⁰

TABLE XXIII

TYPICAL PULPING PROCEDURES FOR MAKING DEINKED STOCK

	No. 1	No. 2
Furnish	Yellow pad paper	Book and magazine
Chemical	1½-2% NaOH 0.5% soap	3% NaOH 0.5% synthetic detergent
Equipment	Beater	Hydrapulper
Temperature	140° F.	185 to 190° F.
Time	Beaten 1½ hours	Pulped ¾ hours
Bleaching conditions	0.5-1% available chlorine on fiber, pH 8.5, 98° F.	0.75-1% available chlorine

In the third method, cooking and defibering are done simultaneously in globe boilers. Dry paper, hot water, and chemicals are fed to the boiler. The consistency is generally in the neighborhood of 25 to 35%, although consistencies as low as 6 to 7% are sometimes used. The temperature of cooking varies from 170 to 200° F., and the time of cooking varies from 3 to 8 hours. Steam is generally introduced directly into the charge by means of a perforated pipe running throughout the width of the boiler.

⁴⁵⁹ H. P. Bailey, A. H. Nadelman and E. F. Andrews, *Tech. Assoc. Papers* 31: 265-269 (June, 1948)

⁴⁶⁰ R. Carr, *Paper Ind.* 31, No. 3: 337-338 (June, 1949)

Heating with saturated steam rather than superheated steam is best, particularly if sodium hydroxide is used as the cooking agent.⁴⁶¹ In extreme cases, as long as 8 to 10 hours at 40 to 50 p.s.i. steam pressure may be used.⁴⁶² This is not the best practice, however, since it results in a loss of yield, due to degradation and solution of the carbohydrates. At the end of the cooking period, the stock is dumped in the form of a pulpy mass to a pit underneath the cooker where the liquor is drained away. In most cases, the liquor is saved for reuse.

Washing of Deinked Pulp

After draining, the stock is mixed with water and defibered in a breaker beater, a circulating tank and pump, or similar device. The next step is washing the pulp, which is a very important part of the deinking process.

Washing may be done in a Hollander beater equipped with a washing cylinder covered with 60- or 70-mesh wire similar to the type of washer used for cooked rags. Fresh water is added to the stock at the same rate that dirty water is removed by the washing cylinders. Washing is best carried out at low consistency and with little pressure on the beater roll, in order to produce the lightest colored pulp. In the better grades, washing is frequently done in countercurrent multistage cylinder washers, usually of the Lancaster type. These are more efficient than washing in the beater and are gradually replacing Hollander beaters. One disadvantage is that the filter mat tends to retain the ink particles.

Large quantities of water are required to wash the pulp thoroughly. Excessive washing has the disadvantages of causing large fiber losses, but pulp which is insufficiently washed will darken when alum is added, on account of the precipitation of suspended impurities on the fibers. Foaming should be held to a minimum, since the foam and froth formed during washing has a strong affinity for carbon black particles. If the foam is allowed to break on the mat of stock, it may deposit particles of carbon, thereby resulting in a darkening of the stock.⁴⁶³ Antifoams are sometimes added to keep down foam.

Shrinkage on washing varies from about 8 to 10% for ledger stock to 20 to 35% for book and magazine stock. The total loss of stock in deinking usually ranges from 15 to 40%. Heavily coated book paper when used alone may result in as much as 40 to 60% shrinkage.⁴⁶⁴ Fiber loss is relatively low when long-fibered ledger stock is used, but is very high when short-fibered, pigment-coated book papers are used.

⁴⁶¹ A. O. Bragg, *Paper Trade J.* 112, No. 17: 207-214 (Apr. 24, 1941)

⁴⁶² F. C. Clark, *Paper Trade J.* 116, No. 13: 147-149 (Apr. 8, 1943)

⁴⁶³ S. D. Wells, *Paper Mill News* 67, No. 20: 12-24 (May 13, 1944)

⁴⁶⁴ R. O'Donoghue, *Paper Ind.* 22, No. 9: 911-916 (Dec., 1940)

Well-washed deinked stock ranges in color from a fairly bright, blue-white for ledger stock to a dull gray when mixed papers are used. In order to whiten the stock, it must be bleached with chlorine. Ordinarily, $\frac{1}{2}$ to 1% chlorine added as calcium hypochlorite is sufficient to whiten the stock. Temperatures of 90 to 120° F. are used to speed up the reaction. In some cases, multistage bleaching methods are used.

Properties of Deinked Stock

Most deinked stock has a slightly grayish cast, because of the small amount of carbon retained by the fibers. The stock is used for much the same purposes as soda pulp and is generally competitive with soda pulp in price. It is used in book papers and in coating rawstock where it improves the bulk, opacity, softness, and formation of the paper. The pulp requires no beating. In fact, beating injures the stock, and for this reason, deinked stock should always be added after the refining when used in mixed furnishes. Ordinarily, the final ash content of deinked stock is in the range of 2.5 to 4.0%. Even excessive washing will not reduce the ash content below about 1.0%.⁴⁶⁵

PULPING OF RAGS

Rags were one of the earliest raw materials used in paper manufacture and, prior to 1860, constituted the only significant source of papermaking fiber. Today, however, rags constitute only a relatively small part of the total raw material used for papermaking because of their limited supply and high cost, compared with wood.

Types of Rag Used

High-grade cotton and linen rags are used for making high-grade writing and bond papers where permanence, high strength, and distinctive quality are of interest. Low-grade rags are used for the manufacture of felts used as a base for floor covering or roofing papers. In addition to rags, the paper industry utilizes other fiber wastes e.g., rope, twine, tent material, and burlap for making strong wrapping papers. This material is generally sold as hard fiber waste, which may contain jute, sisal, manila, caroa, or hemp fibers. The availability of this material depends entirely on market conditions and is likely to vary quite widely.

Rags are obtained in the form of new rags or cuttings from textile or garment factories, and as old rags obtained mostly by house-to-house collection. Cotton rags are most widely used. Linen rags are also used to a considerable extent, but their use is generally limited to expensive bonds,

⁴⁶⁵ H. O. Ware and R. T. Washburn, *Paper Trade J.* 122, No. 26: 283-287 (June 27, 1946)

special tissues, or cigarette papers. Wool or wool-cotton fabrics are undesirable because wool is destroyed by the alkali used in the cooking operation.

Old rags are usually purchased by the paper mill from a rag dealer who collects, partly grades the product, and sells it under a variety of classifications, e.g., old white, thirds, and blues. Further grading at the paper mill is usually necessary in order to eliminate all undesirable material from the product, e.g., wool, rubber, buttons, metal, and leather. Other steps in the preparation of rags for cooking are cleaning, sorting, cutting, and dusting. Hendrick⁴⁶⁶ recommends cutting the rags to the size of cotton flock in order to eliminate one of the variables in the cooking process.

When making white writing papers, the rags should have a good color, be capable of easy bleaching, and have high strength and high alpha cellulose content. Ordinarily, unbleached rag cuttings, such as muslins, make the strongest paper, even after bleaching in the paper mill. Colored rags impose a difficult problem if the rags are to be used in white papers. Colored rags should be graded for bleachability, since some colors are readily removed and others are extremely difficult, if not impossible, to remove without harming the fiber. Since the trend is toward the development of greater color fastness, the problem of cooking colored rag is becoming more difficult all the time. Colored rags having colors known to be hard to remove are saved for dark-color papers.

Another situation making the selection of the proper rags for papermaking extremely difficult has been the increase in the use of synthetic finishes and the use of synthetic fibers. Some of the synthetic fibers which may be present in fabrics alone or in blends include nylon, viscose, cuprammonium, cellulose acetate, and vinyl resin fibers. These synthetic fibers are difficult to process and are not suitable for papermaking. The presence of special permanent finishes on cotton fibers (such as finishes obtained with the vinyl resins, acrylates, urea and melamine formaldehyde resins, and rubber-like derivatives) are objectionable to the papermaker because these finishes cannot be removed by ordinary rag-processing methods. As a result, the rags are incompletely digested in the cooking operation, resulting in bits of rag in the pulp. The detection of synthetic fibers and identification of special finishes is a difficult and painstaking job and presents a very serious problem to the rag mills.

Cooking Conditions in Rag Mills

Rags must be cooked to remove waxes and resinous matter in the fiber, to remove finishing and loading materials added to the fabric, to destroy partially or "start" the color, and to "soften" the fiber. Rotary boilers

⁴⁶⁶ W. G. Hendrick, *Paper Trade J.* 120, No. 17: 163-167 (Apr. 26, 1945)

heated with direct steam are generally used for the cooking of rags. Cooking conditions vary according to the type of rag used.

Cooking is generally carried out in alkaline liquor at pressures ranging from 20 to 40 p.s.i., although pressures up to 50 to 60 p.s.i. are sometimes used. Liquor ratio is about 3 to 1. Cooking time is 2 to 15 hours. Loss of rag in cooking varies, depending upon the quality of the rags and the severity of the cook. Generally, the loss is in the range of 25 to 50% of the original rag.

Chemicals Used in Rag Cooking

Sodium hydroxide, lime, and mixtures of lime and sodium carbonate are the usual chemicals used for the cooking of rags. Lime is generally used in the United States, and sodium hydroxide in England. Rags for saturating felts are sometimes cooked with about 6 to 8% sodium carbonate at a pressure of 30 p.s.i. for a cooking time of about 8 hours. Reducing agents such as hydrosulfite may be employed for decolorizing highly colored rag or rags dyed with fast colors, e.g., dyes of the indanthrene class.

The amount of alkali required depends upon the color and dirtiness of the rags. When used alone, between 3 to 5% sodium hydroxide on the weight of rags is sufficient. More than this amount of sodium hydroxide results in excessive degradation of the fiber. Replacing 20 to 50% of the sodium hydroxide with sodium silicate is said to improve the color and strength of the rags.

Lime is widely used for the cooking of new, white cuttings. It is low in cost, produces a pulp of good color, and less degrading effect on the cellulose than sodium hydroxide. When used as the sole cooking agent, about 5 to 20% or an average of about 15% lime is used on the weight of the rags. The disadvantage of lime is that it produces insoluble reaction products which are difficult to wash from cooked pulp. It also forms insoluble lime salts which tend to fill up the wires and felts on the paper machine.

Mixtures of lime and sodium carbonate are often used, particularly when unbleached or colored rags are being cooked. Generally, the ratio of lime to sodium carbonate is 3–5 to 1. A typical cook on colored rags for making bond paper would be 10% lime and 2% sodium carbonate on the weight of the rags. Mixtures of lime and sodium carbonate provide a more uniform rate of reaction and less injury to the fiber than sodium hydroxide alone.

Cooking of Cotton Linters

Cotton rags have been the principal source of raw material for making rag paper, but recently the use of cotton linters has increased because of the shortage of acceptable cotton rags. Cotton linters are the short fuzzy

fibers which are firmly attached to the cotton seed. They are not removed by ginning, and hence, a special cutting operation is necessary to remove the fibers from the seed.

Cooking is necessary in preparing cotton linters for papermaking in order to remove the oils, waxes, pectates, and other foreign matter in the fiber. Cotton linters are cooked in either vertical stationary or spherical rotary type digesters, using a dilute solution of sodium hydroxide (1.5 to 3.0% solution) to give about 8% sodium hydroxide on the weight of the dry linters. Sometimes a small amount of soap or wetting agent is also added. Cooking is carried out at a pressure of 30 to 100 p.s.i. for 3 to 8 hours. If a high cuprammonium viscosity is desired, as when making dissolving cellulose, low pressures are used. Otherwise, the cooking and bleaching process is very similar to that used in rag pulps. The amount of bleach is much less than that used with wood pulps.

Much of the pulp made from cotton linters is used for the manufacture of cellulose derivatives (e.g., cellulose acetate) and rayon. Some is used in the paper trade for the manufacture of special permanent papers. Care is taken in pulping and bleaching to produce a uniformly pure cellulose of the desired chemical and physical properties. Blending of the pulp is frequently practiced to obtain a final product of the desired properties. Chemical cotton linter pulp is sold in sheet form for the paper and viscose trade and in loose form for use in making cellulose derivatives.

Washing Rag Pulps

The washing of rag pulps is quite different from the washing of wood pulps. Rag washing is carried out in a special machine called a washer which is similar to a Hollander beater, except that a revolving wire-covered drum turns in the stock and removes dirty water at the same rate that fresh water is added. If the rags are cooked in lime, cold wash water is generally used to take advantage of the greater solubility of lime in cold water.

The washer functions not only as a washing machine, but also as a beater, and when the water removed by the cylinder washer is fairly clear, the beater roll is lowered against the bedplate to loosen the remaining dirt and to brush out the rags. Temperature, pH, and hardness of the water are important in rag washing, just as in the washing of chemical wood pulps, but the degree of beating or mechanical action on the fibers is probably of even greater importance. If the beater roll is lowered too soon, the dirt is beaten into the fibers instead of being removed. The total washing period requires about 4 to 10 hours and the pulp is generally washed at a rate of 60 to 100 gal. per minute. The consistency during washing is about 3.5%.

Bleaching is generally done by adding hypochlorite to the partially beaten fibers in the washer. The beating should not be too hard during this

period, since the fibers are in a highly susceptible condition. When bleaching is complete, the pulp, or half-stuff, as it is called, is washed again and removed to storage cells called drainers, where the pulp is stored for a period of 2 to 7 days. During this period, the pulp is "softened." This traditional method of processing rag pulps dates back many hundreds of years without appreciable change.

Characteristics of Rag Pulps

The two principal rag fibers are cotton and linen. Cotton (*Gossypium hirsutum*) consists of long, flat fibers which are twisted. There are about 150 to 300 spirals to the inch, twisting being less pronounced where the cell wall is thickest. The fibers are rounded at one end, but torn at the other end where the fiber was attached to the seed coat. Longitudinal and spiral striations are common. Cotton staple fibers have an average length of about 18 mm. and a diameter of about 20 microns. Cotton linters are shorter and are generally not twisted. The average fiber length of cotton linters is about 6.0 to 7.0 mm. for first-cut linters, 2.0 mm. for second-cut linters, and 3.5 to 5.0 mm. for mill-run linters. Cotton fiber is too long for good formation on the paper machine and generally must be cut in refining. Cotton linters produce pulps of better color and higher alpha cellulose content, compared with cotton rag pulps, but the paper is not so strong as that produced from staple fiber, on account of the tendency of the linters to break up into coarse fibrils, compared with the fine fibrils obtained with staple fiber. The first cut, or longer-fibered linters, make stronger paper than the second-cut linters.

The linen used in linen rags is obtained from the flax plant (*Linum usitatissimum*). Linen fibers are long and slender and have tapered ends. The lumen is very narrow, often appearing as a dark line. Characteristic thickened or node-like swellings exist at intervals along the fiber, and often the fiber is fractured in the transverse direction. The fibers have an average length of about 25 mm. and are about 16 microns in width.

Rag pulps are characterized by a high alpha cellulose content (often as high as 96 to 98%), low copper number, and high cuprammonium viscosity. Because of these characteristics, rag pulps are used for the manufacture of high-grade papers for permanent records. Rag paper is very strong and durable and is the best grade of paper for use where the paper receives considerable handling. Rag pulps are well suited for making lightweight papers containing a high filler content. The cuprammonium viscosity of rag pulps varies from about 10 for pulp which has been overbleached or made from old rags to 300 for lightly bleached pulp made from new rags.

Among the grades of paper which are made from 100% rag or from

part rag and part chemical wood pulp are bonds, ledgers, filter papers, sensitizing papers, Bible paper, high-grade drawing papers, onion skin papers, cigarette papers, carbon tissue, blueprint, lightweight specialties, and vulcanized fiber. Banknote papers are usually made from 75% linen fibers and 25% cotton fibers. Old rags are used in the manufacture of roofing felt, which is later impregnated with asphalt.

PULPING OF CEREAL STRAW

Two distinct types of pulps are made from straw: coarse pulps for paperboards and fine pulps for use in high-grade papers. Coarse straw pulps are produced in yields of 70% or higher, whereas fine straw pulps are produced in yields of 35 to 45%.

Coarse straw pulps for the manufacture of corrugating paper have been produced in the United States for many years, using wheat straw and, to a lesser extent, rye and oat straw. Fine straw pulps suitable for use in fine papers have been produced from wheat and rye straw in Holland, France, Germany, Italy, Belgium, and other European countries where available pulpwood is very limited. Fine straw has not been made in the United States because of (1) the high cost of collecting, handling, and storing straw and (2) the low yields obtained as a result of the low cellulose content of straw compared with wood. Interest in the use of straw pulps in the United States has increased recently, on account of increasing wood costs, improved methods of collecting and storing straws, and improved methods of cooking straw.

Properties of Straws

Straw is a seasonal crop which is available only during the summer and early fall. Most companies purchase their straw within a 50-mile radius of the mill. In order to maintain constant year-round operation, it is necessary to buy straw in bales during the proper season and then store the straw on farm sites or at the mill yards for use in the winter and spring months. Most mills attempt to store at least a four to six months' supply of straw. The straw is stored in stacks about 20 bales high. In some mills, the stacks are left uncovered in the mill yard, whereas in other mills, the stacks may be covered with canvas, sheet metal, or asphalted kraft paper to offset the effects of weathering. Good straw should have less than 5% chaff and be free of weeds, dirt, seeds, and trash.

Normally, the moisture content of straw varies from 8 to 14%, but straws having moistures up to 50% are sometimes obtained. Straw is generally purchased on the basis of dry straw delivered, deductions being made for excess moisture. Too high a moisture content is undesirable because it results in rapid and extensive deterioration of the straw in storage

TABLE XXIV
AVERAGE PER CENT COMPOSITION OF EUROPEAN STRAW

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Sample designation	Total ash	Ether extract	Total protein	Water extract	Insol. ash	Insol. protein	Lignin	Pentosan	Holocel. lulose	Ash in holocel. lulose	Pure holocel. lulose	Ash- and Pentosan- containing a-cellulose		Ash in a-cel. lulose	Pentosan in a-cel. lulose	Pure a-cel. lulose	Remainder
												Per cent of holoc. of straw	Per cent of straw				
Summer barley ...	10.5	1.5	2.5	12.0	2.7	1.4	16.2	27.0	73.9	2.6	71.3	53.4	39.4	1.4	2.0	36.0	3.2
Winter barley	8.7	1.2	2.9	12.3	1.9	1.4	16.9	26.4	72.8	1.8	71.0	54.4	39.5	1.1	1.7	36.7	3.2
Oats heavy soils ..	11.9	1.2	2.5	14.9	2.3	1.3	15.5	26.0	71.7	2.3	69.4	55.0	39.4	1.3	1.8	36.4	2.4
Oats light soils ...	7.4	1.5	2.3	14.8	0.7	1.3	16.7	26.4	70.2	1.2	69.0	54.2	38.0	0.4	2.3	35.4	3.2
Summer wheat heavy soils	11.2	1.2	3.3	12.0	4.4	1.6	16.3	26.2	74.0	4.2	69.9	53.7	39.8	2.8	2.4	34.6	3.7
Summer wheat light soils	5.1	1.4	3.5	13.4	0.9	1.8	17.0	27.0	72.1	1.2	70.9	52.8	38.0	1.2	2.4	34.4	4.1
Winter wheat heavy soils	11.1	1.0	2.5	12.5	4.9	1.5	15.7	27.1	75.0	4.7	70.3	54.0	40.5	3.0	2.4	35.2	2.1
Rye	3.8	1.4	3.5	8.8	0.6	1.6	17.8	27.9	75.5	0.9	74.6	55.8	42.1	0.4	2.5	39.3	2.6
General average ..	8.7	1.3	2.9	12.6	2.3	1.5	16.5	26.8	73.2	2.4	70.8	54.2	39.6	1.5	2.2	36.0	3.0

due to rotting. High moisture also constitutes a fire hazard by promoting spontaneous combustion of the straw. The use of preservatives (e.g., sodium pentachlorophenate and borax) have been suggested for eliminating the rotting of stored straw.⁴⁶⁷ Weathered straw produces a pulp of low strength, and generally the yield is reduced.

Straw has a lower cellulose content than wood, but in spite of its low cellulose content, straw has a total carbohydrate fraction (holocellulose) approximately equal to that of wood.⁴⁶⁸ This is due to the high hemicellulose and low lignin content compared to wood. Ash content is greater than wood. Analyses of European straws are given in Table XXIV,⁴⁶⁹ and of American straws in Table XXV.⁴⁷⁰

TABLE XXV

ANALYSIS OF DIFFERENT AMERICAN STRAWS

(All values except moisture given on per cent basis of moisture-free material)

	Rice straw	Barley straw	Wheat straw	Rye straw	Oat straw	Flax shivs	Soybean stalks
Moisture	8.0	8.4	6.6	7.4	7.0	8.1	8.3
Ash	16.1	6.4	6.6	4.3	7.2	3.5	2.3
Extractives							
Alcohol-benzene	4.6	4.7	3.7	3.2	4.4	4.1	3.9
Cold water	10.6	16.0	5.8	8.4	13.2	9.7	7.3
Hot water	13.3	16.1	7.4	9.4	15.3	11.4	8.8
1% NaOH	49.1	47.0	41.0	37.4	41.8	32.0	32.0
Nitrogen	0.58	1.10	0.38	0.72	0.46	0.69	0.66
Lignin	11.9	14.5	16.7	19.0	17.5	22.3	19.8
Pentosans	24.5	24.7	28.2	30.5	27.1	23.6	24.8
Cross and Bevan cellulose							
Crude	49.8	48.2	54.4	54.9	53.6	48.4	50.1
Ash free	48.6	47.4	53.6	54.3	53.4	46.2	48.2
Pentosans	27.8	30.0	26.8	29.5	28.4	21.6	22.1
Alpha cellulose	36.2	33.8	39.9	37.6	39.4	34.9	34.5

Cereal straws, like all canes and grasses, contain a number of different cells. Straw fibers, which are principally derived from the bast cells in the internodes, are fairly long (about 1.5 mm.), slender fibers with sharply pointed ends. In addition to these fibers, straw also contains short, non-fibrous cells consisting of epidermal cells, platelets, serrated cells and spirals which are derived from the pith, nodes, chaff, and rachises (heads). A considerable portion of the small cells is lost during cooking and washing

⁴⁶⁷ B. F. Stahl and H. L. Smith, *Tech. Assoc. Papers* 31: 577-579 (June, 1948)

⁴⁶⁸ G. J. Ritter and E. F. Kurth, *Ind. Eng. Chem.* 25: 1240-1253 (1933)

⁴⁶⁹ E. L. Ritman, F. M. Muller and J. G. Dijkhuis, *Paper Ind.* 29, No. 12: 1751-1754 (Mar., 1948)

⁴⁷⁰ S. I. Aronovsky, G. H. Nelson and E. C. Lathrop, *Paper Trade J.* 117, No. 25: 258-268 (Dec. 16, 1943)

of straw pulps. This reduces the yield, but is desirable from the standpoint of improved pulp quality.

Soft winter wheat straw and rye straw are preferred over other straws. Rye straw has a higher cellulose content and somewhat longer fibers than other straws. Oat straw cooks readily, but it has a shorter fiber length and tends to make a soft paper. Barley straws cook with more difficulty than wheat or oat straw, principally because of the "beards" which are not reduced in the cooking liquor. Wheat and rye straws produce stiffer, stronger papers than other straws.

Pulping Processes Used on Straw

A number of different chemicals are used for pulping straw. These are: (1) sodium hydroxide, (2) lime alone or in combination with other alkalies, (3) sodium sulfite plus other alkali, and (4) chlorine. Other chemicals suggested for the pulping of straw are nitric acid and sodium chlorite. Sodium carbonate plus sulfur has been suggested for the preparation of a coarse pulp (straw kraft) used for corrugating papers.⁴⁷¹

Straw is almost universally cooked in rotary digesters. Recently, however, a mechano-chemical process using a hydropulper has been developed by the Northern Regional Research Laboratory. In the conventional method of cooking in rotary digesters, as practiced in the United States, the straw is taken directly from the storage piles and dumped into digesters after removing the baling wire. In European mills, the straw is generally cut to lengths of 2½ to 3 in. before being fed to the digesters, which increases the capacity of the digester by about 10%. After passing through the cutter, the chopped straw is dropped into a hopper below the cutter, and from there is sucked into a cyclone separator where the loose fines and dust are drawn out through a screen at the top.⁴⁷² Screens, riffles, and vortraps are used for removing the nodes and remaining dirt from the cooked pulp.⁴⁷² If high-grade pulp is being made, the straw from the cyclone may be given an additional cleaning by threshing and screening to remove the nodes and additional fines, but lower yields are obtained than by the previous method. Recently, American mills have become interested in the use of roll-type fiber presses for cutting straw prior to cooking. Treating in this way cracks the nodes and rachises of the straw and allows for faster penetration of the cooking chemical.⁴⁷³

Conditions used for cooking straw vary widely in different mills. Since straw is very sensitive to cooking reagents, the conditions of cooking must not be too severe if excessive loss in yield is to be avoided. The

⁴⁷¹ S. D. Wells, U. S. 1,626,171 (Apr. 26, 1927)

⁴⁷² J. E. Atchison, *Tappi* 33, No. 3: 42A, 44A, 48A, 50A, 52A (Mar., 1950)

⁴⁷³ L. F. Herman, *Tappi* 33, No. 6: 262-263 (June, 1950)

strongest pulps are produced by the soda process, followed by the sulfate, and then by the neutral sulfite. Yields are in the reverse order.⁴⁷⁴ The acid sulfite pulping process is not suitable for cooking straw because the pulps produced make weak, brittle papers.

Coarse Straw Pulp Made by Lime Process

Lime is the most widely used chemical for the cooking of coarse straw pulps in the United States and Europe, particularly for strawboard and low-quality straw wrapping paper. Dolomite lime is preferred. Most strawboard in the United States is produced in the midwestern states, Ohio, Indiana, Illinois, Kansas, Iowa, Wisconsin, and Michigan, using mostly wheat straw and some rye and oat straw.

Lime can be used as the sole cooking agent, or a small amount of sodium hydroxide or sodium carbonate may be used in combination with the lime. By replacing part of the lime with these other alkalies, a stronger and stiffer pulp is produced and liming-up of the mill equipment is reduced. When used alone, between 8 to 12% ordinary lime or 12 to 18% dolomite lime is generally used on the weight of the straw. When used in mixture with other alkalies, about 5 to 10% lime on the weight of the straw is used. The liquor ratio is generally about 3 or 3.5 to 1.

In cooking with lime, some mills use a one-fill system in which the straw, chemical, and water are put into the digester at the beginning and the digester is not opened until the end of the cook. Other mills make two to six fills of straw, leaving about twenty minutes between each fill to permit "wilting." This increases the capacity of the digester.

After the digester is filled, the charge is heated with direct steam. Cooking is continued at a temperature of about 110 to 120° C. for a period of 6 to 12 hours while the digester turns at the rate of one revolution every 3 to 6 minutes. There is usually considerable false pressure built up in the digester, but generally there is no venting of gases after the last fill is made. Cooking is carried out to the point of softening the nodes of the straw. The yield of pulp is generally about 70 to 85% of the dry straw.

After cooking, the straw may be discharged into drainers and held there for a period of about 48 hours to allow the chemical to drain away and to soften the straw further,⁴⁷⁵ after which the pulp is beaten or refined. In some cases, the draining period is omitted, the pulp being sent directly from the digester to the beaters and/or refiners. The pulp may be washed after refining, or it may be sent directly to the paper machine with all the fines and residual chemicals present. When making better grades of corrugating

⁴⁷⁴ S. I. Aronovsky, A. J. Ernst, H. M. Sutcliffe and G. H. Nelson, *Tech. Assoc. Papers* 31: 299-304 (June, 1948)

⁴⁷⁵ W. W. Galloway, *Paper Ind.* 19: 415-421 (July, 1937)

paper, it is customary to wash the straw during beating by means of a washing cylinder in order to remove the residual alkali and part of the debris from the pulp. In some cases, the pulp may be further washed on vacuum filters. Some insoluble salts (e.g., calcium carbonate) are generally left in the pulp, and these tend to deposit on the paper machine wires and felts.

If beaters are used, it is customary to beat no longer than about 70 minutes, since longer beating is harmful to the fiber, tending to produce fiber fines and reducing the yield.⁴⁷⁶ The ash content of the pulp is about 10 to 15%, depending upon the amount of washing. After beating, the pulp is usually jordaned. Thorough refining is necessary to break up the nodes which, if not thoroughly digested and disintegrated, tend to rise to the surface of the paper, forming long black streaks when the paper is calendered.⁴⁷⁷ Recently, there has been interest in the use of disk mills for the refining of straw pulp. Disk mills produce a slightly stronger pulp at higher freeness than conventional refining methods.⁴⁷⁸ Trouble with fouling of the mill results when long stems are present, but this can be eliminated by a two-stage refining process in which the first stage operates as a break-down stage and the second as a controlled refining stage.

Coarse Straw Pulp by Mechanical Pulping

Straw can be cooked in a hydropulper at atmospheric pressure at a temperature near 100° C. with no added chemical to produce a very coarse pulp suitable for strawboard.⁴⁷⁹ The cooking time ranges from ½ to 1½ hours, and the consistency is about 10%.

Recent work at the Northern Regional Research Laboratory has indicated that insulating boards of very high impact strength can be made from wheat straw by first preparing fiber bundles from the straw and then mixing a portion of those long-fibered bundles with a portion of cooked, well-hydrated straw filler pulp.⁴⁸⁰ The long-fibered component is cooked without chemical (water to straw ratio of 6 to 1, temperature of 142° C., and 1.25 hours cooking time), after which the pulp is put through a coarse screen and refined in a disk refiner at a plate clearance of 0.025 in. The pulp is then screened into long-fibered fractions and blended with chemically cooked straw.

Pulping of Straw with Sodium Hydroxide

High-quality pulps can be made from straw when sodium hydroxide is used as the cooking agent. About 12% sodium hydroxide is the minimum

⁴⁷⁶ B. F. Stahl, *Tech. Assoc. Papers* 31: 217-220 (June, 1948)

⁴⁷⁷ W. W. Galloway, *Paper Ind.* 19: 415-421 (July, 1937)

⁴⁷⁸ C. K. Textor and L. E. Eberhardt, *Tappi* 33, No. 4: 193-194 (Apr., 1950)

⁴⁷⁹ S. I. Aronovsky and E. C. Lathrop, *Tappi* 32, No. 4: 145-149 (Apr., 1949)

⁴⁸⁰ E. C. Lathrop and T. R. Naffziger, *Tappi* 32, No. 2: 91-96 (Feb., 1949)

practical amount of chemical required to produce a satisfactory pulp.⁴⁸¹ Aronovsky and coworkers⁴⁸²⁻⁴⁸⁴ produced a high-quality pulp from wheat straw by cooking for 2 hours at 170° C. with 12 to 15% caustic soda at a liquor ratio of 7 to 1, the minimum quantity of liquid necessary to cover the packed straw.

The effect of increasing amounts of sodium hydroxide on the yield and chemical properties of wheat straw is shown in Table XXVI.⁴⁸⁵ It can be seen from this table that increasing the amount of sodium hydroxide from 10.5 to 16.8% decreased the yield of crude pulp, but had little effect on the yield of screened pulp. Increasing the amount of chemical decreased the bleach requirement and increased strength of the pulp. The response of

TABLE XXVI

EFFECT OF SODIUM HYDROXIDE ON WHEAT STRAW
(Cooking temperature 170° C., time 2 hours, liquor ratio of 7 to 1)

Amount of chemical, % NaOH	Yield of pulp		Ash, %	Pentosans, %	Lignin, %	Chlorine consump- tion, %
	Crude, %	Screened, %				
10.5	53.0	41.1	5.2	29.2	7.6	11.4
12.0	51.9	40.5	4.4	26.1	6.2	11.5
14.0	49.4	39.8	3.1	30.9	4.7	8.6
16.8	45.1	38.7	2.3	28.3	2.7	3.7

different straws to cooking with a constant amount of sodium hydroxide (12%) is shown in Table XXVII.⁴⁸⁶

The sodium hydroxide and the sulfate processes have been used commercially in Europe for the production of fine straw pulps. About 14 to 15% sodium hydroxide on the air-dry weight of the straw is used. Cooking is carried out in rotary boilers at about 40 p.s.i. for approximately 2 to 4 hours. The yield of bleached pulp is between 35 to 42%. During World War II, considerable straw was cooked in England in esparto mills equipped with stationary digesters. This method of handling was not very satisfactory, and the best yields of pulp (bleached) which could be obtained were of the order of 30 to 35%.

⁴⁸¹ S. I. Aronovsky, A. J. Ernst, H. M. Sutcliffe and G. H. Nelson, *Tech. Assoc. Papers* 31: 299-304 (June, 1948)

⁴⁸² S. I. Aronovsky, G. H. Nelson and E. C. Lathrop, *Paper Trade J.* 117, No. 25: 38-48 (Dec. 16, 1943)

⁴⁸³ S. I. Aronovsky, Alan Rhodes and E. C. Lathrop, *Paper Trade J.* 124, No. 13: 49-55 (Mar. 27, 1947)

⁴⁸⁴ S. I. Aronovsky, A. J. Ernst, H. M. Sutcliffe and G. H. Nelson, *Paper Trade J.* 126, No. 26: 289-294 (June 24, 1948)

⁴⁸⁵ S. I. Aronovsky, A. J. Ernst, H. M. Sutcliffe and G. H. Nelson, *Tech. Assoc. Papers* 31: 299-304 (June, 1948)

⁴⁸⁶ S. I. Aronovsky, G. H. Nelson and E. C. Lathrop, *Paper Trade J.* 117, No. 25: 258-268 (Dec. 16, 1943)

Special pulpers have been suggested for making fine straw pulp by simultaneous chemical and mechanical treatment at atmospheric pressure in a process called the mechano-chemical process. Aronovsky and Lathrop⁴⁸⁷ suggest the use of 12% of sulfate cooking liquor for making fine straw pulp in the hydrapulper. Pulps having a yield of about 50% can be obtained in $\frac{1}{2}$ to 1 hour, the rapid rate of pulping in this process being due to the mechanical action which increases the diffusion of active chemical and reaction products into and out of the straw.

Atchison⁴⁸⁸ describes a unique pulping process used in Italy whereby the straw is treated with about 10% sodium hydroxide and allowed to stand in chests for about 15 days. The pulp is admirably suited for the manufacture of glassine paper because of the high hemicellulose content resulting from the mild digestion.

TABLE XXVII

PROPERTIES OF ALKALINE-COOKED STRAWS

(Amount of NaOH used 12% on oven-dry material, time of cooking 2 hours, cooking pressure 100 p.s.i., liquor ratio 8 to 1)

	Rice straw	Wheat straw	Barley straw	Rye straw	Oat straw
Pulp yield					
Crude, %	48.2	53.8	46.1	53.1	52.4
Screened, %	35.7	34.5	29.4	33.6	39.1
Screenings, %	2.2	11.0	5.1	5.8	2.7
Ash, %	15.8	2.9	4.3	2.8	2.7
Lignin, %	3.5	5.1	5.4	3.8	3.9
Permanganate number	10.6	17.7	16.7	14.7	13.1
Roe chlorine number	2.3	4.5	4.6	3.1	3.4

When making fine straw pulps by the sodium hydroxide process, it is desirable to recover the alkali for reuse. One difficulty in recovery is the high proportion of silica in the straw. This silica reacts with the alkali to form silicates which interfere with settling in causticization and cause encrustation of the evaporators and furnaces. Because of the difficulties involved, alkali recovery is often not practiced in straw mills, and when it is, recovery of alkali is generally low, i.e., 65 to 80%.

Pulping of Straw with Sodium Sulfite

Sodium sulfite was suggested for the pulping of straw many years ago, but has never had extensive use because the amount of chemical required and the cost were believed to be prohibitive. Some sodium sulfite has been used in small amounts to replace lime in the cooking straw for coarse pulps.

⁴⁸⁷ S. I. Aronovsky and E. C. Lathrop, *Tappi* 32, No. 4: 145-149 (Apr., 1949)

⁴⁸⁸ J. E. Atchison, *Tappi* 33, No. 3: 42A, 44A, 48A, 50A, 52A (Mar., 1950)

When used in small proportion mixed with other alkalies (e.g., sodium hydroxide, sodium carbonate, or lime), sodium sulfite results in some improvement in rigidity and a reduction in washing time required in the beaters.⁴⁸⁹ Rue and Monsson⁴⁹⁰ were able to produce straw pulps superior in yield and strength to ordinary lime-cooked straws by cooking with 7.5% sodium carbonate and 1.5% sodium sulfite on the weight of the straw.

Recent work at the Northern Regional Laboratory has shown that it is possible to produce satisfactory pulps from straws by pulping in a liquor containing sodium sulfite as the major chemical. The action is less drastic than obtained with the caustic alkalies. The effect of increasing amounts of sodium sulfite on the pulping of wheat straw is shown in Table XXVIII.⁴⁹¹ Excellent pulps of corrugating grade can be produced from wheat straw by cooking with 10% sodium sulfite alone, 4% sodium sulfite plus 2% sodium hydroxide, or 2% sodium sulfite plus 4% sodium carbonate.⁴⁹² The presence of other alkalies with sodium sulfite improves the yield, strength, and brightness of the pulp.⁴⁹³

TABLE XXVIII

PULPING OF WHEAT STRAW WITH SODIUM SULFITE
(Temperature 170° C., cooking time 2 hours, lignin ratio 7 to 1)

Amount of sodium sulfite, %	Pulp yield		Ash, %	Pentosans, %	Lignin, %	Chlorine consump- tion, %
	Crude, %	Screened, %				
7.9	57.8	49.9	8.3	23.3	10.7	22.7
9.4	56.1	50.2	8.4	23.0	8.9	12.4
11.0	57.2	51.5	8.6	25.5	5.7	8.0
12.6	55.6	49.2	9.6	24.4	4.3	6.7
13.7	57.4	49.9	8.6	28.1	3.9	5.2

In Italy, high-grade straw pulp is produced commercially, using 10% sodium sulfite and 5% sodium hydroxide on the dry weight of the straw.^{494, 495} The straw is cooked for about 8 hours at 160° C., after which the pulp is very thoroughly screened and then bleached. The final yield of bleached pulp is about 42% of the dry weight of straw received, the rather low yield being due to the large amount of material removed in cleaning.

⁴⁸⁹ G. S. Hannaway, *Paper Trade J.* 126, No. 9: 126-128 (Feb. 26, 1948)
⁴⁹⁰ J. D. Rue and W. Monsson, *Paper Trade J.* 80, No. 15: 146-147 (Oct. 8, 1925)
⁴⁹¹ S. I. Aronovsky, A. J. Ernst, H. M. Sutcliffe and G. H. Nelson, *Tech. Assoc. Papers* 31: 299-304 (June, 1948)
⁴⁹² H. M. Sutcliffe, S. I. Aronovsky, R. M. Wilkinson, W. D. Burnham, W. A. Phillips and E. R. Carpenter. Paper given at 35th Annual Meeting TAPPI, New York, N. Y. (Feb., 1950)
⁴⁹³ S. I. Aronovsky, G. H. Nelson, H. A. Ernst, H. M. Sutcliffe, and E. C. Lathrop, *Tech. Assoc. Papers* 31: 291-299 (June, 1948)
⁴⁹⁴ J. E. Atchison, *Tappi* 33, No. 1: 46-48 (Jan., 1950)
⁴⁹⁵ J. E. Atchison, *Tappi* 33, No. 3: 42A, 44A, 48A, 50A, 52A (Mar., 1950)

In a proposed neutral sulfite process for producing high yield, high-quality pulp, the straw is chopped into short lengths (1.5 in.), screened, and then cooked with 8% sodium sulfite plus 2 to 3% sodium carbonate (on the dry straw basis) at a liquid-to-solid ratio of 7 to 1 for 2 hours at 170° C. (100 p.s.i.). The cook is blown at 40 lb. pressure, which serves to disintegrate the uncooked nodes.⁴⁹⁶ The pulp can be bleached with about 5 to 7% chlorine to a brightness of 70 at a yield of 50 to 52%. The resulting pulp hydrates rapidly because of its high hemicellulose content and has a bursting strength in the neighborhood of commercial softwood sulfite pulp. The pulp can be mixed with other chemical wood pulps in the manufacture of writing, mimeograph, and book papers.

Pulping of Straw with Chlorine

In Italy, France, India, the Philippines, Mexico, South Africa, Argentina, and other places, the Pomilio chlorine process has been used for the pulping of straws. The Pomilio process is a continuous multistage pulping process utilizing weak caustic soda solution and chlorine in about the same proportion that these chemicals are produced by electrolytic decomposition of sodium chloride. The process consists of the following steps: (1) predigestion of the raw material with weak alkali at moderate temperatures for a short period; (2) treatment of the digested, washed mass with moist chlorine gas in the cold; (3) treatment of the water-washed chlorinated mass with weak alkali; (4) treatment of the washed mass with hypochlorite.⁴⁹⁷

A recent modification of the Pomilio process is the Celdecor-Pomilio process which is based upon more modern equipment and operating conditions.⁴⁹⁵ In this process, the straw is treated with about 8% sodium hydroxide (on the weight of the straw) in a mixing machine, and then the wet straw is transported to a reaction tower about 50 to 60 ft. high where the straw slowly settles while it is heated by means of steam jackets. The retention time in the tower is about 1½ hours for bleachable pulp, but less for coarse pulp used for making board and wrapping paper. If bleachable grades are being made, the digested and washed pulp is chlorinated with about 18% chlorine in a tower where the chlorine enters through pipes around the wall. Before entering the chlorination tower, however, the pulp is run through a special machine which fluffs the pulp and exposes a large surface area. This operation is essential to obtain uniform chlorination.⁴⁹⁸ After chlorination, the pulp is washed, extracted with about 0.4% caustic (on pulp weight), washed again, screened to remove nodes and seeds, and

⁴⁹⁶ E. C. Lathrop, *Pulp Paper Mag. Canada* 50, No. 3: 167-178, Convention Issue (1949)

⁴⁹⁷ V. Pomilio, *Ind. Eng. Chem.* 31, No. 6: 657-662 (June, 1939)

⁴⁹⁸ J. Strachan, *Paper-Maker* 116, No. 1: 11-12, 14 (July, 1948)

finally is bleached with hypochlorite, using 3% chlorine based on pulp weight.

The cost of the Pomilio process is based upon the amount of salt used and the electric power required to convert the salt into alkali and chlorine. In the original Pomilio process, the consumption of salt was about 540 kg. for rice straw, or about 600 kg. for wheat straw per ton of pulp. Consumption of current was about 1,100 kw.-hr. per ton, and steam consumption was about 1.2 to 1.5 tons per ton of pulp.⁴⁹⁹ More efficient operation is obtained by the more modern design and conditions used in the Celdecor-Pomilio process. Yields of pulp are reported to be about 45%.

Pulping of Straw with Other Reagents

Straw can be pulped by many processes in addition to those described above, but for the most part, the results are not commercially feasible. Two pulping agents not used commercially, but which are worth of mention, are sodium chlorite and nitric acid.

Pulps of good strength can be produced from grain-straw by cooking in a solution containing 8% sodium chlorite on the weight of the straw after the straw has been extracted with alkali to remove silicious matter.⁵⁰⁰ Pulps in yields of 49 to 56% can be prepared by digesting in sodium chlorite acidified to a pH of 2.5 for a period of 24 to 48 hours at 50° C.⁵⁰¹

Nitric acid produces a high-quality pulp from straw. A 2.0 to 5.0% solution of nitric acid is sufficient to reduce straw to a suitable pulp⁵⁰² in a period of about 4 to 6 hours at a temperature of 90° C.

Properties of Straw Pulps

The properties of straw pulps depend upon the type of straw and the conditions of cooking. In general, straw pulps beat very rapidly and are slower than wood pulps. The slowness of straw pulps is due partly to overcooking and partly to the presence of incompletely disintegrated fine platelets and cells which originate from the nodes and rachises of the straw.⁵⁰³ Freeness can be increased by washing the pulp to remove the debris.

When produced in yields of 35 to 37% (screened yield) by the soda process, straw pulps are approximately equal in strength to softwood sulfite pulps in all properties except tearing resistance.⁵⁰⁴ The fibers are short,

⁴⁹⁹ *World's Paper Trade Rev.* 109, No. 6: 450-454 (Feb. 11, 1938)

⁵⁰⁰ G. P. Vincent and J. F. White, *Paper Ind.* 27, No. 7: 1038-1039 (Oct., 1945)

⁵⁰¹ G. P. Vincent, *Paper Ind.* 27, No. 6: 880-881, 884 (Sept., 1945)

⁵⁰² Through a review by S. I. Aronovsky, J. David Reid, E. C. Dryden, E. R. Whittemore and D. F. J. Lynch, *Paper Ind.*, (Apr., May, June, 1939)

⁵⁰³ S. I. Aronovsky, *Paper Ind.* 32, No. 1: 88-90 (Apr., 1950)

⁵⁰⁴ S. I. Aronovsky, A. Rhodes and E. C. Lathrop, *Paper Trade J.* 124, No. 13: 133-139 (Mar. 27, 1947)

averaging about 1.5 mm. in length, but the ratio of fiber length to fiber diameter is high.

High-grade straw pulps produce papers having good formation and good surface properties. These pulps are suitable for use in writing and printing papers when mixed with a high proportion of chemical wood pulps. They can be used in high proportion in such grades as glassine and greaseproof. They are not suited for bag and wrapping papers for which high tearing resistance is a requirement.

High yield, coarse straw pulps are used in the manufacture of corrugating paper, egg case filler board, and other grades of coarse papers. Ordinary strawboard for corrugating is yellowish brown in color and has a thickness of 0.009 in. and a weight of 28 to 32 lb. per 1,000 sq.ft. The high stiffness and smooth surface of the paper makes it desirable for corrugating medium. The stiffness of straw papers is related to the high hemicellulosic content of the pulps, and is determined by the conditions used in cooking the straw. In some grades of corrugating medium, about 10% kraft softwood pulp is mixed with the straw to increase the tearing strength.

PULPING OF ESPARTO

Esparto (*Stipa tenacissima*) is a reed-like grass which grows abundantly in Spain and northern Africa. The plant, which grows to an ultimate height of 3 to 4 ft., consists of two parts, a hard stem, and soft blades, which are from 0.5 to 3.0 ft. in length. In harvest, the blades are pulled from the stems by hand, the roots and stems being left to provide a new crop. The blades are dried and shipped in bales to England and France where they are used for the manufacture of pulp.

The first step in pulping of esparto is loosening of the bales and cleaning. Cooking is carried out in upright stationary digesters equipped with liquor circulating equipment. Sodium hydroxide is the usual cooking agent, and from 10 to 15% on the weight of the grass is usually added. The time of cooking varies from 2 to 5 hours and the pressure from 30 to 65 p.s.i. The yield is about 40 to 45%. After cooking, the pulp is washed to remove the spent liquor, which is then recovered in the alkali recovery plant. Next, the pulp is screened, washed again, and finally bleached. Ordinarily, esparto pulp is low in strength. However, if cooked under mild conditions, a high yield pulp (i.e., about 60%) can be prepared from esparto having a strength approaching coniferous sulfite pulp in strength.⁵⁰⁵

Esparto pulp is similar in properties to soda pulp from hardwoods. The fibers are somewhat shorter than those in straw, averaging about 1.1 mm. in length, but the ratio of fiber length to fiber width is higher than

⁵⁰⁵ M. B. Shaw, G. W. Bicking and R. R. Rumsey, *Paper Trade J.* 81, No. 12: 119-120 (Sept. 17, 1925)

that for straw. The fibers may be either thick or thin walled. An identifying characteristic of esparto is the presence of small, pear-shaped trichomes (17 by 30 microns) which are hooked at the apex. Papers made from esparto are characterized by high opacity, softness, and excellent formation. Esparto pulp is used principally for high-grade printing papers for which it is admirably suited.

Esparto can be pulped by the sulfate, the neutral sulfite, or the Pomilio process. Sodium sulfite produces pulp in higher yield than the soda process.⁵⁰⁶

PULPING OF HEMP

Bast fibers are present in hemp in the form of fiber bundles underneath the bark. These fiber bundles are separated from the hemp by retting and mechanical separation to produce fiber suitable for the manufacture of textiles, rope, and similar materials. Some hemp straw is used directly in papermaking, but the principal source of hemp fiber for papermaking is old rope and cordage collected by junk dealers and sold to the paper mill.

There are three principal hemp fibers: the true hemp (*Cannabis sativa*), Manila hemp (*Musa textilis*), and sisal hemp (*Agave*). The true hemp (*Cannabis sativa*) contains fibers having an average length of about 20 to 22 mm. and a width of about 22 microns. The cell cavity is wide, and the walls have striations in the longitudinal direction and fractures in the transverse direction. Manila hemp (*Musa textilis*) fibers are much shorter, having an average length of about 6 mm. and an average width of about 18 microns. Sisal (*Agave*) has longer fibers than manila hemp. The fibers are tapered and pointed at the ends and are stiff. The walls are thick and have many fine cross lines. Manila hemp is the principal hemp fiber used in papermaking, although some true hemp (*Cannabis sativa*) is used in Europe for making Bible, cigarette, and other thin papers.

Most paper containing manila hemp is made from old rope collected at seaports and inland shipping ports and is sold to the mill as waste. Cooking is necessary to remove the natural waxes, loosen up the dirt, and soften the fiber. Before cooking, the raw material is cut into lengths of about 2 in. by means of a heavy cutter. Cooking is generally done in rotary boilers, using about 10% lime and 5% sodium carbonate on the weight of the fiber. If the raw material is contaminated with oil and grease, special treatment may be necessary. Ordinarily, the pressure of cooking is in the neighborhood of 25 p.s.i. and the time of cooking about 8 to 10 hours. The yield of fiber is in the range of 50 to 65%. Bidell⁵⁰⁷ recommends cooking

⁵⁰⁶ J. d'A. Clark, *Pulp Paper Mag. Canada* 24: 815 (July 15, 1926)

⁵⁰⁷ G. A. Bidell, U. S. 1,531,728

in a special beater, using 11 to 14% lime and 0.1% or less of sodium hydroxide. After beating, the pulp is washed in the same way as rag washing. Much hemp is used unbleached, but for some purposes the pulp is bleached with hypochlorite.

Hemp pulp beats readily and produces papers which are exceptionally strong and pliable. It is used in making special bag paper, special wrapping papers, cable-insulation paper, pattern paper, sandpaper, tags, gaskets, carbon papers, and other grades where exceptional strength and toughness are required.

PULPING OF JUTE

Jute (*Corchorus capsularis* and *Corchorus olitorius*) is a fast-growing annual of India. The fibers in jute average about 2 mm. in length and about 20 microns in diameter. The fiber cavity is wide in spots, but it is constricted by joints at intervals so that the cell cavity is almost blocked. The fiber wall is smooth and the fiber is tapered at the ends. The primary use for jute is for cordage, twine, and burlap. Some jute has been pulped in the form of the whole plant, but the principal source of jute fiber for paper-making is old jute bagging and burlap.

Cooking of waste jute is necessary to remove the natural waxes, dirt, loading, and other impurities. Before cooking, jute must first be inspected, cut to length, and dusted. It is then cooked in rotary digesters, using from 8 to 15% lime on the weight of dry jute. The cooking pressure is generally 20 to 30 p.s.i., and the time of cooking 8 to 12 hours. The yield is usually 60 to 65%. The cooked stock is washed and bleached in the same way as for rag pulp.

Jute pulp has a bright yellow color. Average fiber length of jute is about 2.0 mm. Papers produced from jute have good strength, and the principal uses are for special bag, wrapping, and drawing papers.

PULPING OF FLAX

Flax is grown extensively in Europe for use in the textile industry for the manufacture of linen fabrics. The bast fibers are separated from the woody part of the stem by retting and mechanical processing to produce long, strong fiber bundles used for weaving. Considerable seed flax is grown in the United States, primarily for the manufacture of linseed oil. Some flax fiber reaches the paper mill in the form of linen rags obtained from waste rags, spinning wastes, threads, or similar sources. This is converted into high-grade pulp suitable for fine papers by cooking with sodium carbonate or sodium hydroxide.

Seed flax straw has been suggested as a source of papermaking fiber. Flax in straw form is a more difficult raw material than waste linen fiber,

since it contains the same long fibers found in linen and, in addition, contains woody cells, epidermal cells, and small vessels. Many processes have been suggested for the pulping of flax straws, although few have any commercial importance. Most of the suggested processes are based upon the use of alkalies, e.g., sodium hydroxide,^{508, 509} sodium hydroxide plus sodium sulfide, sodium carbonate,⁵¹⁰ lime, trisodium phosphate,⁵¹¹ and sodium sulfite.⁵¹² Other cooking chemicals suggested are chlorine^{513, 514} and nitric acid.

Some seed flax straw is used in Canada and the United States in the manufacture of cigarette paper and other thin papers requiring high strength, e.g., air mail, bonds, and banknote papers. The raw straw is decorticated by running through breakers consisting of fluted rollers which crack the woody straw and produce about 20% of "fine tow" on the weight of the straw. The tow is then screened, put up in bales of about 140 lb., and shipped to the paper mill. The tow, as received, consists of about 20% bast fiber and 70% wood fiber.

Cooking of seed flax straw is generally done in globe digesters using 16 to 20% sodium hydroxide on the weight of the fiber. The cooking temperature is about 350° F. Sodium sulfate may be used for part of the make-up chemical.

After cooking and washing, the pulp is chlorinated and finally bleached with hypochlorite. The yield is from 25 to 60%, depending upon the cleanliness of the straw.⁵¹⁵

PULPING OF BAGASSE AND CORNSTALKS

Bagasse is the fibrous residue left after the crushing and extraction of sugar cane (*Saccharum officinarum*). Bagasse has been used extensively for the production of coarse insulating board. It contains fibers averaging about 1.7 mm. in length and about 20 microns in diameter. In addition, there are many smaller cells of the parenchyma type, epidermis, and vessel segments. Bagasse has the advantage over other agricultural waste as a source of papermaking fiber in that there is no problem of collection, since it exists as a by-product of sugar mills. There is, however, the necessity of

⁵⁰⁸ G. A. Lowry and J. A. Grant, U. S. 2,064,929 (Dec. 22, 1936)

⁵⁰⁹ C. C. Heritage, E. R. Schafer and L. A. Carpenter, U. S. 1,922,366 (Aug. 15, 1933)

⁵¹⁰ C. Ruzicka and C. V. Sale, Brit. Pat. 502,451 (Mar. 17, 1939)

⁵¹¹ F. R. Chesley, U. S. 2,073,682 (Mar. 16, 1937)

⁵¹² M. W. Bray and C. E. Peterson, *Ind. Eng. Chem.* 19, No. 3:371-372 (Mar., 1927)

⁵¹³ V. Pomilio, *Ind. Eng. Chem.* 31: 657 (1939)

⁵¹⁴ R. H. McKee, U. S. 1,932,904 (Oct. 31, 1933)

⁵¹⁵ H. S. Spencer, *Pulp Paper Mag. Canada* 47: 95-97, Convention Issue (1946)

weighing the value of bagasse as a papermaking raw material against its value as a fuel for the sugar mill.

The steps involved in the cooking of bagasse are: (1) cutting the bagasse into short pieces, (2) cooking in the presence of water, and (3) refining the pulp. The yields are very high and production costs are low. Sugar cane bagasse is particularly well suited to the manufacture of insulating boards because of its long, springy fiber bundles.

There have been many attempts to make high-quality pulp from bagasse, but in most cases the results have been unsuccessful. However, high grade bleached pulp is being produced from bagasse by the Celdecor-Pomilio process in the Philippines, and India, and new mills are planned in other countries, e.g., Brazil and South Africa.⁵¹⁶ Optimum conditions for making high-quality pulp from bagasse by the soda process as determined by Lynch and Goss⁵¹⁷ are 25% sodium hydroxide, liquor ratio of 5 to 1, cooking time of 6 hours, and cooking pressure of 125 p.s.i. Under these conditions, a good bleachable pulp in yield of 34 to 35% was obtained. Sodium sulfite can be used alone but high chemical ratios are required; a small amount of sodium sulfite in a soda cook improves the yield.

The nitric acid process is suitable for pulping bagasse. A bleachable pulp in high yield (42 to 46%) can be obtained from bagasse by steeping in a 5% solution of nitric acid for 3 hours at room temperature, or for 1 hour at 80° C.⁵¹⁸ About 70% of the acid is recoverable by draining. Approximately 15% nitric acid is consumed in the cooking of bagasse.

Recent work at the Northern Regional Research Laboratory has shown that excellent pulp for fine papers can be produced from sugarcane bagasse from which the pith has been largely removed by a relatively simple method. This separation method produces two products—bagasse pith relatively free from fiber, and bagasse fiber relatively free from pith. It is proposed to use the pith mixed with sugarcane molasses for the production of balanced ration stock feeds, with the addition of protein, vitamins, and so on. The other product, the relatively pith-free bagasse fiber, is much more suitable than whole bagasse for the production of pulp for fine papers. It produces larger yields of pulp with considerably improved properties over that obtained from whole bagasse. The depithed fiber can be processed in present mill equipment by any of the alkaline processes or it can be transformed into pulp by the mechano-chemical process previously referred to.

The stalks from corn (*Zea mays*) are similar to bagasse and can be used for making approximately the same type of paper. The same type of

⁵¹⁶ *Southern Pulp and Paper Mfg.* 13, No. 6: 40-42 (June 15, 1950)

⁵¹⁷ D. F. J. Lynch and M. J. Goss, *Ind. Eng. Chem.* 24, No. 11: 1249-1254 (Nov., 1932)

⁵¹⁸ D. F. J. Lynch and M. J. Goss, *Ind. Eng. Chem.* 24, No. 11: 1249-1254 (Nov., 1932)

fibers and small cells are present, except that the corresponding cells are somewhat smaller in corn than in bagasse. One difficulty is the high percentage of pith cells which are undesirable, since they tend to produce a rattly, translucent paper. In order to overcome this objection, Wells⁵¹⁹ has proposed a two-stage process by which the pith cells are removed from the bast fibers by screening.

The major obstacle that must be overcome in the commercial utilization of cornstalks for pulp and paper purposes is the economic one of collecting and storing these stalks for year-round operation. Until suitable economic means for collecting and storing these cornstalks are developed, this material can have no particular interest to the pulp and paper industry.

PULPING OF BAMBOO

Bamboo (*Dendrocalamus arundinacea*) is a grass which grows profusely in Burma, India, Siam, Indo-China, and the Philippines. It has received considerable attention as a papermaking material because of its rapid growth. Recently, attempts have been made to grow bamboo experimentally in the southern part of the United States.

Bamboo is reproduced annually (flowering at 30- to 65-year intervals), but the roots are perennial. Growth is rapid, but full-sized stems are not produced until the seventh to tenth year. Bamboo varies in size according to the species. Some species are small (0.5 to 1.0 in. in diameter and 12 to 20 ft. in height), whereas other species are large (8 in. in diameter and 150 ft. in height). Chemically, bamboo contains four principal substances, starches, pectins, lignins, and celluloses.

The bamboo stem consists of (1) a woody portion or hollow tube, referred to as the culm and (2) the ground tissue or parenchyma. In the ground tissue, there are fibrovascular bundles. The fibers are similar to sugar cane and corn. The parenchyma cells are smaller, however, and there are some very wide, thin-walled fibers in addition to the regular fibers.

The woody portion or culm of the bamboo stem is jointed at nodes along the length. These nodes constitute a problem in pulping, since they are denser than the rest of the stalk and hence are penetrated with greater difficulty. The cooking of bamboo is facilitated by crushing the bamboo stems between heavy iron rollers which crush the internodes and separate the fiber bundles.⁵²⁰ This makes the fibers more accessible to the cooking liquor, which is an important factor in the pulping of bamboo, since there are no horizontal ray parenchyma to conduct the liquor horizontally into the stems.

⁵¹⁹ S. D. Wells, U. S. 2,029,973 (Feb. 4, 1936)

⁵²⁰ M. P. Bhargava and C. Singh, *Paper Trade J.* 128, No. 8: 63-69 (Feb. 24, 1949)

Alkaline cooking processes are best suited to bamboo, the sulfate process being best. High-grade bleachable pulps can be made from bamboo by the sulfate process.⁵²¹ About 20 to 22% chemical on the weight of the bamboo is required. The maximum pressure should be about 120 lb., temperature 162 to 170° C., and the time of cooking about 5 to 6 hours. The yield is about 41 to 43%. A two-stage process involving the countercurrent use of alkali has been found to be highly advantageous.⁵²² One proposed process involves steeping of the bamboo in spent liquor from an earlier cook for 2 to 2.5 hours at 115 to 120° C., followed by cooking in a 5% solution of NaOH for 2 more hours at 140 to 160° C.⁵²³

⁵²¹ *Paper Mill News* 72, No. 31: 11-12 (July 30, 1949)

⁵²² W. Raitt, *The Digestion of Grasses and Bamboo for Papermaking*. Crosby, Lockwood and Son, London (1931)

⁵²³ Unpublished thesis by M. A. Joglekar (Sept., 1949), "The Solubility of Bamboo as a Raw Material for the Manufacture of Dissolving Pulp." State Univ. of N. Y. College of Forestry, Syracuse, N. Y.

BLEACHING

Pure cellulose is white, but commercial cellulose contains impurities which are never completely removed in the pulping process and which impart color to the pulp. Unbleached pulps are unsuited for the manufacture of high-grade, white papers. The chief objective in bleaching is the production of a white pulp of stable color obtained at reasonable cost and a minimum deleterious effect on the physical and chemical properties of the pulp. The principal bleaching and purifying agents used are chlorine and hypochlorite. Other bleaching agents used in smaller quantities are peroxide, chlorine dioxide, and chlorite.

The cost of removing lignin is less in the cooking process than in the bleaching process, and for this reason, it is more economical, when making high brightness pulps, to cook to an "easy bleaching" pulp than to attempt the bleaching of a "raw" or undercooked pulp. Bleaching takes up where cooking leaves off in the purification of pulp to a product of the desired color and quality. In one sense, bleaching may be considered to be a continuation of the cooking process, since both are generally concerned with purification. Bleaching complements the cooking process by continuing the purification with a greater degree of selectivity. Because bleaching is carried out on the loosely adhesive fibrous mass, the bleach liquor has free access to each individual fiber. This is in contrast to the cooking process where the cooking liquor must penetrate the chips. Because of this difference, bleaching is far more uniform in its purification than cooking. In some processes, it is almost impossible to make a sharp distinction between cooking and bleaching. For example, chlorination has been suggested for the purification of pulps which have been only partially digested in alkaline or acid cooking liquors. In such a process, the chlorine might well be considered as a pulping chemical, rather than a bleaching agent. Sodium chlorite has also been suggested as both a cooking and a bleaching agent.^{1a}

Two principal reactions take place upon bleaching: (1) solubilization and removal of the colored matter and (2) changing the colored matter to a colorless form. Lignin is the principal colored matter in the pulp. It is removed in some bleaching processes and in others it is simply decolorized.

^{1a} M. C. Taylor and J. F. White, U. S. 1,894,501 (1933)

Excessive bleaching causes chemical degradation of cellulose, and consequently bleaching conditions must be chosen to hold degradation to a minimum. Bleaching agents differ in their degrading effect on cellulose, as manifested by differences in their oxidation potentials, shown in Figure VI.^{1b} It is generally believed that cellulose is not appreciably degraded by oxidizing agents with oxidation potential lower than about 0.9 volt, although the impurities are oxidized at much lower potentials.

Each commercial pulp has its own particular peculiarities which must be taken into account in bleaching. Each pulp should be bleached in accordance with its individual requirements in order to develop the desired qualities without sacrificing other good characteristics of the pulp. Differences in bleaching properties are ascribable to differences in the amount and nature of the encrusting materials. These are a function of the species of

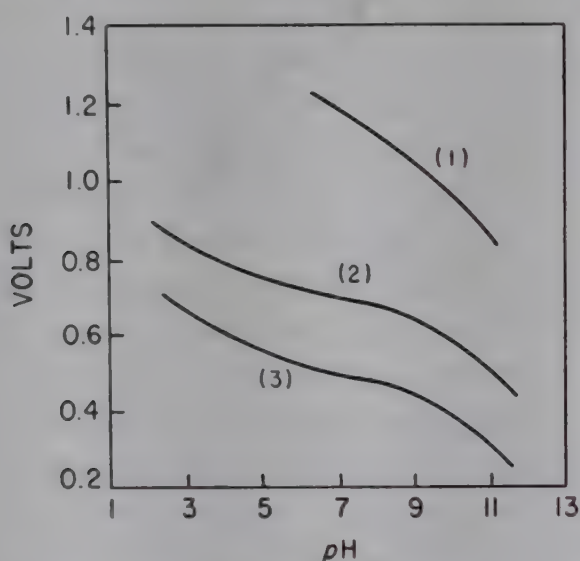


Fig. V-1. Oxidation potentials of hypochlorite (1), chlorite (2), and peroxide (3) referred to the normal hydrogen electrode.

wood used, type of cooking agent used, and severity of the cooking operation. Groundwood, for example, contains practically all the original wood substance and therefore requires a bleaching procedure different from that used on chemical pulps. The bleaching of wood pulps presents a more difficult problem than the bleaching of rags, because it is necessary, in the case of wood pulps, to remove significant amounts (1–8%) of non-cellulosic materials. Lawrence¹ found that thoroughly dried pulps bleach more readily than slush pulps presumably due to the migration of coloring matter to the surfaces of the fibers during drying where it is more readily accessible to the bleaching agent. Another explanation is that drying results in some reversion in brightness which is fairly easily recovered on bleaching. Sulfite pulps bleach more readily than sulfate pulps probably because the residual

^{1b} L. E. Russell, *Paper Ind.* 28, No. 4: 528–531 (July, 1946)

¹ W. P. Lawrence, *Paper Trade J.* 124, No. 21: 230–232 (May 22, 1947)

lignin in sulfite pulps has been rendered partially soluble by the action of sulfite cooking liquor.

In general, chemical wood pulps are bleached with chlorine compounds, either direct chlorine plus hypochlorite, or hypochlorite alone. Semichemical pulps may be bleached with chlorine compounds or with peroxide. Groundwood pulps are generally bleached with peroxide, but hardwood groundwood pulps can be bleached with hypochlorite. The various processes are discussed in the following sections. Rag pulps and deinked papers are generally bleached with hypochlorite, and since there are no particular problems encountered with these pulps, the following discussion is limited to wood pulps only. The bleaching of colored broke for use in white papers is a problem which sometimes arises. Laughlin and Lips² found that approximately 40% of the dyestuffs used in papermaking are readily bleachable with hypochlorite.

Originally, bleaching of wood pulp was carried out in a single operation, but since the introduction of hard-bleaching pulps, stepwise purification or multistage bleaching has become popular. Single-stage bleaching with calcium hypochlorite is still practiced for rag and easy-bleaching, moderate brightness wood pulps, but most wood pulps are now bleached by multistage processes involving chlorination, calcium hypochlorite bleaching, and in-between alkali or water-washing stages. Modern bleaching of wood pulps involves a stepwise purification of the pulps in the first step of which a large part of the coloring matter is rendered soluble, and after these soluble products have been washed away, the remaining coloring matter is oxidized to a colorless form and the pulp is washed again.

Complete purification of wood pulps is not necessary for most grades of paper. In fact, it is desirable for most papermaking purposes that the pulp contain some hemicellulosic material. In addition to this hemicellulosic material, commercially bleached papermaking pulps generally contain some ash and a small amount of lignin. On the other hand, pulps to be used for the manufacture of cellulose derivatives such as rayon must be highly purified. The special steps which are taken for the purification of cellulose for cellulose derivatives are described later in this chapter. Typical analyses of bleached soda, sulfate, and sulfite pulps have been given in the chapter on pulping (see Tables VI and XV). An analysis of special purified pulp is given later in this chapter (see Tables XV and XVI).

Bleachability of Pulp

Of the several tests for determining the bleachability of a pulp or, in other words, the capacity of the pulp to bleach to a given whiteness, the most important are the hypochlorite bleachability test, chlorine number, and per-

² E. M. R. Laughlin and H. A. Lips, *Paper Ind.* 22, No. 6: 557-562 (Sept., 1940)

manganate number. A description of these tests is given in the following sections. When making bleachability tests on samples of pulp taken from the digester, the pulp should be screened to remove knots and shives, and the pulp should be washed thoroughly to remove cooking liquor. Special stains are sometimes used to determine the approximate degree of fiber purification (see microscopical analysis of paper).

Tests for bleachability are useful because (1) they furnish an estimate of the amount of bleach required in the bleaching operation and (2) they serve as a guide and control for the cooking operation. It should be pointed out that bleachability tests do not correlate absolutely with commercial bleach demand when different pulps are considered, although the relationship is fairly valid when the same pulp is used. Factors, curves, or charts must be used to convert bleachability tests into commercial bleach demand.

Bleachability tests are useful on unbleached pulps as an indication of the strength and ease of beating of the pulp³ because of the relationship between bleachability and hemicellulose content for a given pulp. Generally speaking, a low bleachability for a given pulp means that the pulp is highly purified and will not beat as readily as the same type of pulp containing more hemicellulosic matter. If the bleachability is extremely high as in a very raw, undercooked pulp, the pulp is said to be "hard" and as a rule will not develop strength on beating. An intermediate bleachability value is the most desirable for easy-beating pulp.

When pulps of the same origin are considered,⁴ there is a fair correlation between the lignin content of unbleached pulps and the bleachability of the pulp. Pigman and Csellak⁵ obtained a linear relationship between lignin content and bleach requirement to attain a brightness of 85 for both sulfite and sulfate pulps. However, for a given lignin content, sulfate pulps are much more difficult to bleach, especially at the higher levels of lignin contents. Kress and Voigtman⁶ have shown a straight-line relationship between the bleachability as measured by per cent chlorine and the lignin content in the case of sulfite pulp having from 0.3 to 1.6% lignin. Fuller⁷ has also shown that permanganate number bears a straight-line relationship to lignin content in the range of 4 to 8% lignin in the case of sulfate pulp. Bray and coworkers⁸ showed a similar relationship between Roe chlorine number and lignin content for sulfate (pine) pulp. There also appears to be

³ N. S. Grant, O. A. Mason and H. F. Donnelly, *Pulp Paper Mag. Canada* 48: 151-158, Convention Issue (1947)

⁴ H. Raichberg, *Papier-Fabr.* 29: 491-497, 516-524, 535-541 (1931)

⁵ W. W. Pigman and W. R. Csellak, *Tech. Assoc. Papers* 31: 393-399 (June, 1948)

⁶ O. Kress and E. H. Voigtman, *Paper Trade J.* 97, No. 7: 29-44 (Aug. 17, 1933)

⁷ R. R. Fuller, *Paper Trade J.* 112, No. 4: 41-44 (Jan. 23, 1941)

⁸ M. W. Bray, J. S. Martin and S. L. Schwartz, *Paper Trade J.* 105, No. 24: 347-352 (Dec. 9, 1937)

a straight-line relationship between the lignin content and the permanganate number, Roe chlorine number, and bleach requirement in the case of straw pulps.⁹ Permanganate number is inadequate, however, as a means of indicating the lignin content of pulp which has been partially bleached.¹⁰

Hypochlorite Bleachability Test

The hypochlorite bleachability is the amount of hypochlorite required for a given weight of pulp to obtain a standard brightness in a single-stage bleaching. Either sodium or calcium hypochlorite can be used in determining the bleachability. It is a measure of the single-stage chlorine demand of the pulp which, to an experienced bleacher, indicates the per cent chlorine required to raise the brightness to a standard value for any bleaching process conditions. When correction factors are applied, the bleach requirement is of great value in indicating the ease of bleaching of rag and sulfite pulps. The test is of less value in the case of sulfate pulps because of the number of steps involved in bleaching sulfate pulps.

In measuring bleach requirement, several samples of pulp are placed in one-quart glass jars, diluted with water to a definite consistency, and a calculated volume of bleach liquor is added. The samples are then shaken well and placed in a thermostatically controlled bath at either 35 or 55° C. and shaken at frequent intervals. It is important that the pulp be free of hard lumps which do not break up readily. After carrying out the bleaching reaction, samples of pulp are removed from the bottles, washed, and made into sheets, which are then air-dried. Brightness measurements are then made as soon as possible. The amount of bleach required for a brightness of 75 (or other standard value) is computed from plots of brightness and chlorine consumption.

There are two methods of measuring bleach requirement, the exhaustion method and the excess bleach method. In the exhaustion method, the samples are left in the water bath until only a light blue color is obtained when a drop of starch-iodide indicator is added. At this point, the bleach is practically exhausted, and the samples are removed and washed. It is essential that a trace of chlorine be still present when the pulp is washed, since complete exhaustion of the chlorine tends to produce a reversion in color. In this method of testing, the percentage bleach consumed and the time for exhaustion of bleach should be included in the report.

The excess bleach method is more rapid than the exhaustion method. In this method, the reaction is allowed to proceed for a definite length of time, at the end of which the amount of chlorine actually consumed is de-

⁹ S. I. Aronovsky, G. H. Nelson and E. C. Lathrop, *Paper Trade J.* 117, No. 25: 258-268 (Dec. 16, 1943)

¹⁰ P. A. Forni, *Paper Trade J.* 119, No. 11: 108-112 (Sept. 14, 1944)

terminated by back-titration. The test is carried out in the same manner as the exhaustion bleach method except that the samples are left in the water bath for a time of four hours only, after which they are removed and washed on a Buchner funnel until no chlorine remains in the pulp. The washings are collected and treated with acetic acid and an excess of potassium iodide. The iodine released from the potassium iodide by the residual chlorine is then titrated with 0.1 *N* sodium thiosulfate, adding a small amount of starch indicator toward the end of the titration. The amount of chlorine consumed is determined from the difference between the total amount of chlorine added to the pulp and the amount of chlorine in the collected filtrate.

Chlorine Number

The chlorine number, sometimes called the Roe chlorine number, indicates the number of grams of gaseous chlorine absorbed in fifteen minutes (or 5 minutes) at 20° C. by 100 g. (O.D. basis) of pulp at a moisture content of 55%. In this test, disintegrated pulp in the air-dry form is steamed and then chlorinated with chlorine gas in a special apparatus.¹¹ A correction factor is generally applied, using results obtained on a blank of pure pulp.

Another test for chlorine consumption is a measurement of the volume of chlorine absorbed from a chlorine-water solution.

Permanganate Number

Permanganate number is another method of expressing the bleachability of pulp. This test is suitable for both chemical pulps and groundwood and is widely used in control work.

Permanganate number is determined as the number of milliliters of 0.1 *N* potassium permanganate absorbed by 1 g. of moisture-free pulp under certain specified conditions of time, temperature, and acidity. In carrying out this test, the required volume of 0.1 *N* potassium permanganate (either 20 or 40 ml., depending upon the "rawness" of the pulp) is measured into one beaker, an equal volume of 4 *N* sulfuric acid is measured into a second beaker, and enough water is combined with the sulfuric acid so that in the final reaction mixture the permanganate will be 1/300 *N*. When the reagents are ready, the pulp specimen is added to the reaction beaker, followed by the addition of sulfuric acid and then by the addition of permanganate. After exactly 5 minutes at 25° C., an excess of potassium iodide is added to stop the reaction. The residual permanganate in the mixture releases an equivalent weight of iodine from the iodide salt, which is titrated with 0.1 *N* sodium thiosulfate in the reaction beaker without filtering out the fibers, using starch as the indicator. The permanganate number is obtained by subtracting the number of milliliters of 0.1 *N* sodium thiosulfate

¹¹ See TAPPI Standards

from the number of milliliters of 0.1 *N* potassium permanganate originally added and dividing by the moisture-free weight of the test specimen. Bourgon¹² found that a 0.1 difference in permanganate number is brought about by a variation of 1° C. in temperature, a difference of 15 seconds in time, and a difference of 1 ml. of sulfuric acid. When the test is made with proper accuracy, readings can be duplicated within experimental error.

Permanganate number can be converted into approximate equivalent chlorine for bleaching by use of the proper factor for the pulp under consideration. In general, there is good agreement between permanganate number and other methods of measuring bleachability. A conversion chart for converting from one bleachability test to the other is given in Table I.¹³ Mitchell and Yorston¹⁴ found the following relationships to exist between the Roe-Genberg chlorine number and the permanganate number, equation *A* being used for 20 ml. of permanganate, and equation *B* being used for 40 ml. of permanganate.

(*A*) Permanganate No. $\rightarrow 4.0 + 3.25$ (chlorine number)

(*B*) Permanganate No. $\rightarrow 11.5 + 2.20$ (chlorine number)

These equations give results which differ somewhat from those in Table I.

TABLE I
COMPARISON CHART FOR BLEACHABILITY METHODS

(Sulfite pulp)

Permanganate number	Roe chlorine number	Bleach requirement	Permanganate number	Roe chlorine number	Bleach requirement
4	0.7	1.79	10	2.3	4.75
5	1.0	2.26	11	2.7	5.29
6	1.2	2.74	12	3.1	5.82
7	1.5	3.23	13	3.5	6.39
8	1.7	3.72	14	3.9	6.94
9	2.0	4.24	15	4.3	7.52

Easy bleaching pulps have a permanganate number of 6 to 10 or less; medium bleaching pulps a permanganate number of 10 to 14; hard bleaching pulps 14 and up. A pulp with a permanganate number of 20 or above is generally considered as commercially unbleachable.

Composition and Behavior of Chlorine-Water Systems

Because chlorine and chlorine compounds are the best established and most widely used bleaching agents, it is advisable to discuss the general

¹² R. Bourgon, *Pulp Paper Mag. Canada* 47: 125-128, Convention Issue (1946)

¹³ Taken from TAPPI Data Sheets

¹⁴ C. R. Mitchell and F. H. Yorston, *Pulp Paper Mag. Canada* 48, No. 9: 83-85 (Aug., 1947)

chemistry of chlorine-water systems before taking up the specific use of chlorine bleaching agents.

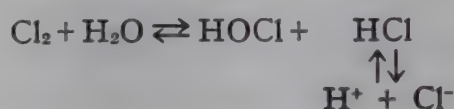
The pH of chlorine-water systems is of the utmost importance and is the secret of chlorine use. The pH determines the relative amounts of molecular chlorine, hypochlorous acid, and hypochlorite ion which are present. Below a pH of 2, molecular chlorine is present substantially alone. From pH 2 to 5, the amount of hypochlorous acid increases until approximately 100% hypochlorous acid is present at a pH of 5. At higher pH values, the concentration of hypochlorite ion increases until, at a pH of 9, substantially all the chlorine is present in the form of hypochlorite ion. The effect of pH on the composition of chlorine-water systems is shown in Table II¹⁵ for a temperature of 25° C. and at a concentration of 0.0225 M .

TABLE II

COMPOSITION OF AQUEOUS CHLORINE SOLUTIONS AT DIFFERENT pH VALUES

(Mole %)				
pH	Cl_2	$HOCl$	OCl^-	Cl^-
2	49.1	50.9	...	193
3	7.5	92.5	...	166
4	0.5	99.5	...	157
5	...	99.5	0.4	155
6	...	96.5	3.6	152
7	...	72.2	27.0	138
8	...	21.2	78.6	118
9.5	...	0.9	99.0	109
11	...	0.1	99.9	107

The complete equation for a chlorine-water system is as follows:



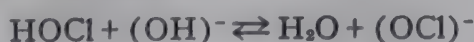
The equilibrium constant K in the reaction

$$K \rightarrow \frac{(H^+)(Cl^-)(HOCl)}{(Cl_2)}$$

is very small in acid medium, indicating that chlorine exists mostly in the molecular, undissociated state. Lowering the pH increases the amount of free chlorine because of the following reaction:



On the other hand, increasing the pH increases the amount of hypochlorite ion, because of the following reaction:



The equilibrium constant for this equation is 10.0×10^{-7} at 25° C.¹⁶

¹⁵ J. N. Swartz, *Pulp Paper Mag. Canada* 47: 203-220, Convention Issue (1946)

¹⁶ F. G. Soper, *J. Chem. Soc.* 125: 2227-2231 (July 4, 1924)

Because pH determines the relative proportions of molecular chlorine, hypochlorous acid, and hypochlorite ion in chlorine-water systems, it determines the relative amounts of chlorination and oxidation which occur in pulp treated with chlorine. In acid solution, both chlorination of the lignin and oxidation of the lignin take place, but chlorination is far more predominant than oxidation.¹⁷ In alkaline medium, the reaction is believed to be predominantly oxidation. Hibbert and Austin¹⁸ found, in reacting hypochlorous acid with isolated lignin, that only 15% of the chlorine was consumed in oxidation under acid conditions, whereas 65 to 75% of the chlorine was consumed in oxidation under alkaline conditions.

A correlation exists between the oxidation potential and the rate at which chlorine is consumed by pulp.¹⁹ Chlorine and hypochlorous acid are more active bleaching agents, i.e., have a higher oxidation potential, than hypochlorite, as shown in Table III. Hence the activity of chlorine-water is greater at low pH than at high pH because of the greater proportions of

TABLE III

REACTIONS AND NORMAL OXIDATION POTENTIALS OF CHLORINE IN DIFFERENT FORMS

Form of chlorine	Reactions involved	Oxidation potential, volts
Hypochlorite ion	$H_2O + OCl^- + 2e = Cl^- + 2OH^-$	+0.94
Elemental chlorine	$\frac{1}{2}Cl_2 + e = Cl^-$	+1.35
Hypochlorous acid	$H^+ + HOCl + 2e = Cl^- + H_2O$	+1.50

Reference:



molecular chlorine and hypochlorous acid which are present. Hibbert and coworkers²⁰ found that the rate constant for the oxidative reaction between chlorine and liginosulfonic acid varies from 0.04 at pH 2 to 0.001 at pH 10. As the pH is decreased from about 10 to 5, the oxidation potential increases in a linear fashion in agreement with the increase in concentration of hypochlorous acid and decrease in concentration of hypochlorite ion which occurs when the pH is lowered in this range. Below a pH of 5.0, the oxidation potential begins to decrease slightly with decreasing pH , on account of an increase in the ratio of chlorine, which has a slightly lower oxidation potential than hypochlorous acid.

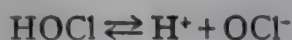
¹⁷ W. R. Carmody and J. S. Mears, *Paper Trade J.* 106, No. 20: 292-294 (May 17, 1938)

¹⁸ H. Hibbert and K. H. Austin, *Can. J. Research* 4: 240-253 (1931)

¹⁹ W. O. Hisey and C. M. Koon, *Paper Trade J.* 103, No. 6: 86-93 (Aug. 6, 1936)

²⁰ E. V. White, J. N. Swartz, Q. P. Peniston, H. Schwartz, J. L. McCarthy and H. Hibbert, *Paper Trade J.* 113, No. 24: 299-309 (Dec. 11, 1941)

Bleaching in the region of pH 6 to 7 is very rapid, but it is difficult to direct the reaction selectively toward the impurities. The major constituent of the chlorine-water system at this pH is hypochlorous acid, which ionizes slightly as follows:



with an ionization constant:

$$K = \frac{(H^+)(OCl^-)}{HOCl} = 3.7 \times 10^{-8}$$

at $18^\circ C$.²¹ If bleaching is done in this pH range, there is rapid degradation of the cellulose, as manifested by an increase in copper number and alkali solubility, and a decrease in viscosity of the pulp.^{22,23} The loss in cuprammonium viscosity of rag pulp bleached with chlorine (hypochlorite) at different pH values is shown in Figure V-2.²⁴

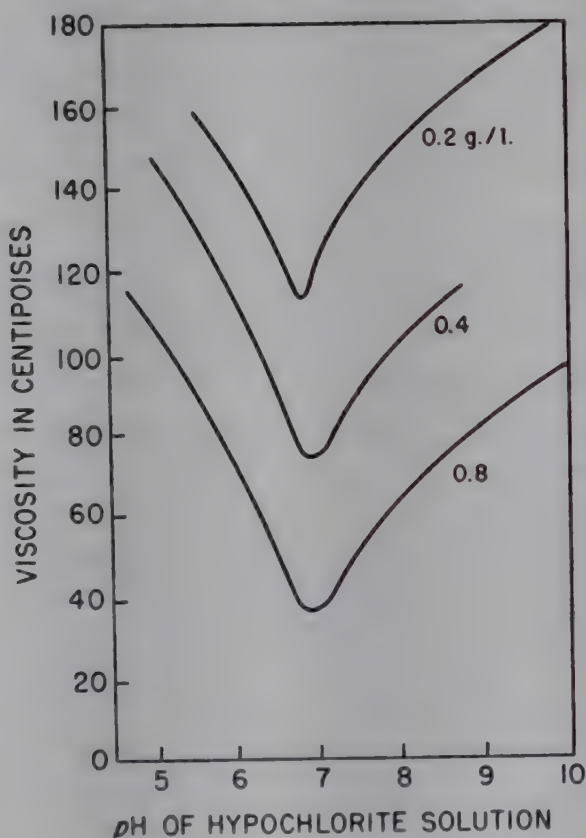


Fig. V-2. Effect of pH of hypochlorite solution on viscosity of rag stock when bleached at three different concentrations.

Preparation of Hypochlorite Bleach Liquor

Nearly all the hypochlorite bleach used by the paper industry is calcium hypochlorite. Very little sodium hypochlorite bleach liquor is used for

²¹ G. F. Davidson, *Shirley Institute Memoirs* 12: 6 (1933)

²² J. N. Swartz, *Pulp Paper Mag. Canada* 47: 203-220, Convention Issue (1946)

²³ R. C. Crain, *Paper Trade J.* 103, No. 24: 343-352 (Dec. 10, 1936)

²⁴ R. C. Crain, *Paper Trade J.* 103, No. 24: 343-352 (Dec. 10, 1936)

ordinary papermaking grades, principally because of the higher cost. The use of sodium hypochlorite is warranted for bleaching dissolving pulps where the greater solubility of the end products is a factor in reducing the ash content of the pulp.

At one time, commercial bleaching powder was the standard source of bleach in paper mills, but today most mills make their own bleaching agent from chlorine. Bleaching powder, which is made by absorbing chlorine in slaked lime, contains roughly 33 to 38% available chlorine. The powder is dissolved in water at a temperature of about 80° F. to produce a solution of calcium hypochlorite, which is then separated by decantation from the sludge of excess calcium hydroxide. Care should be taken to see that the liquor is thoroughly settled, since "muddy" liquor is undesirable. Solid bleaching powder deteriorates rapidly if wet or damp; it should be protected from moisture in shipment and storage:

All large mills make their own bleach liquor by running chlorine gas into a milk of lime suspension in concrete tanks to produce a solution containing about 20 to 35 g. of available chlorine per liter. The reaction in making bleach liquor is expressed by the following equation:



Chlorine is passed into the lime suspension until a pH of 11.2 to 11.5 is reached, because at this point, the lime has been used effectively and the bleach liquor is stable. The proper end point can be determined by adding a few drops of phenolphthalein, which should produce a pink color that disappears in about 3 seconds. For each pound of chlorine absorbed, between 1.15 to 1.20 lb. of hydrated lime, or 0.87 to 0.90 lb. of quicklime, are required.²⁵ Lime is soluble in bleach liquor in the ratio of 1 lb. per 100 gal. of bleach liquor (30 g./l.),²⁶ and dissolves up to a pH of about 12.5, but no more dissolves after that pH is reached. Excess lime is necessary for the following reasons: (1) to stabilize the available chlorine, (2) to neutralize the carbon dioxide and organic acids formed by oxidation during the bleaching reaction, (3) to aid in controlling the bleaching reaction within the desired pH range.

After chlorinating to the proper point, the bleach liquor is generally settled for 4 to 8 hours to remove sludge, after which the clear, greenish yellow bleach liquor is siphoned to storage tanks. In some mills, unsettled bleach liquor is used. Properly made bleach liquor is fairly stable for about 48 hours. The liquor is decomposed on storage by heat, light, and air, and should be protected as much as possible from these influences. The rate of decomposition increases about 2.5 times for each 18 to 20° F. rise in tem-

²⁵ F. Casciani and A. Heilborn, *Paper Ind.* 17, No. 11: 810-814 (Feb., 1936)

²⁶ F. Casciani, *Paper Ind.* 25, No. 4: 427-430 (July, 1943)

perature, the self-decomposition appearing to follow a second order reaction.²⁷ One of the products of decomposition may be sodium chlorate, which is produced according to the following reaction:



Decomposition in this way lowers the *pH*, which progressively speeds up the reaction. In strongly alkaline solutions, chlorate formation is negligible below 40° C.

Certain metallic salts, e.g., iron, copper, nickel, cobalt, and manganese, increase the decomposition of bleach liquor. Metal tanks, pumps, and pipelines which are made from any of the above metals tend to cause decomposition of bleach liquor when clean. However, a coating of rust or lime offers some protection.

Analysis of Bleach Liquor. There are three important chemical tests made on bleach liquor: available chlorine, total chlorine, and alkali content. The methods of making these tests are described below.

The test sample of bleach liquor is agitated and 50 ml. pipetted into a 250-ml. volumetric flask.

*Available Chlorine*²⁸

Pipette 25 ml. of prepared liquor into a 250-ml. flask containing about 25 ml. of water. Add 10 ml. of 20% potassium iodide and 10 ml. of 20% acetic acid and titrate with 0.1 *N* sodium thiosulfate. Add starch indicator near the end point and continue the titration until the disappearance of the blue color.

$$\text{ml. } 0.1 \text{ N Na}_2\text{S}_2\text{O}_3 \times 0.7092 \rightarrow \text{grams available Cl per liter}$$

Total Chlorine

Add 25 ml. of prepared sample to a 250-ml. flask. Add a 3% solution of hydrogen peroxide until effervescence ceases, and then add a few drops of concentrated nitric acid. Add chloride-free calcium carbonate, 0.5 ml. of potassium chromate indicator, and boil until a permanent yellow color is obtained. Titrate with 0.1 *N* silver nitrate to a faint orange tint.

$$\text{ml. } 0.1 \text{ N AgNO}_3 \times 0.7092 \rightarrow \text{grams total Cl per liter}$$

Titratable Alkali

Pipette 50 ml. of test sample into a beaker containing about 100 ml. water. Add neutral 3% hydrogen peroxide solution until all bleach is converted (test with starch-KI paper). Then titrate with 0.1 *N* HCl to a permanent pink color with methyl orange, and then add 5 ml. of 0.1 *N* HCl and back titrate with 0.1 *N* NaOH to a yellow color.

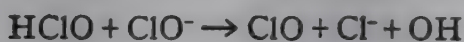
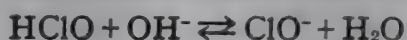
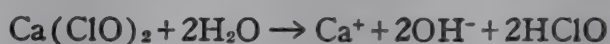
$$\text{ml. } 0.1 \text{ N HCl consumed} \times 0.370 \rightarrow \text{grams titratable alkali per liter}$$

²⁷ E. V. White, J. N. Swartz, Q. P. Peniston, H. Schwartz, J. L. McCarthy and H. Hibbert, *Paper Trade J.* 113, No. 24: 299-309 (Dec. 11, 1941)

²⁸ This method is based upon the fact that, in the case of calcium hypochlorite, two chlorines are present for each oxygen. The results give just twice the amount of hypochlorite available for bleaching.

Single-Stage Bleaching with Hypochlorite

Single-stage bleaching with hypochlorite is one of the oldest bleaching processes. In this process, properly prepared hypochlorite liquor is added to the pulp under the proper conditions and allowed to react until the pulp reaches the desired degree of whiteness. Hypochlorite bleaching is mainly an oxidation which decolorizes and solubilizes the lignin, natural dyes, and other impurities in the fiber. Under certain conditions, reactions other than oxidation predominate. Hypochlorite preferentially attacks lignin, but also reacts with cellulose, particularly if the reaction is not properly controlled. The following reactions are believed to occur in alkaline hypochlorite bleaching:²⁹



Effect of pH in Hypochlorite Bleaching

In single-stage bleaching, using unbuffered hypochlorite, the pH of the mixture decreases during the course of the reaction. Starting with bleach at a pH between 8.5 to 11.0, the pH decreases (rapidly at first, and then more slowly) as bleaching proceeds, because of the formation of carbon dioxide and organic acids, and the fact that hypochlorite (an alkaline salt) is converted into calcium chloride (a neutral salt). The total reaction products of hypochlorite bleaching consist of about 75% carbon dioxide and about 25% organic acids.³⁰ At the end of bleaching, the pH is usually between 6.0 to 7.0. Lower pH values are obtained the farther the bleaching is carried. This changing pH during bleaching results in poor control of the reaction which, in turn, results in degradation of the cellulose, with a consequent weakening of the fiber, and increases the bleach requirement of the pulp.³¹ The undesirable reactions obtained in bleaching in the pH range of 6 to 7 are apparently caused by the great activity of the hypochlorous acid obtained in this pH range, and possibly to a catalytic effect which the hypochlorous acid has on the decomposition of hypochlorite.

Hypochlorite bleaching is best carried out at a pH level such that the active bleaching agent is predominantly hypochlorite, not hypochlorous acid. In order to avoid the undesirable effects of low pH during bleaching, it is customary, in commercial hypochlorite bleaching, to use buffered hypo-

²⁹ M. W. Phelps and J. Schuber, *Paper Trade J.* 106, No. 8: 81-84 (Feb. 24, 1938)

³⁰ H. Rashback and F. H. Yorston, Forest Prod. Lab., *Canadian Pulp and Paper Quarterly Rev.* No. 7: 12-16 (July-Sept., 1931)

³¹ F. Casciani and G. K. Storin, *Paper Trade J.* 115, No. 21: 265-269 (Nov. 19, 1942)

chlorite containing an excess of lime to neutralize the acids and carbon dioxide formed during bleaching. The effect of excess lime content on pH during the course of the bleaching reaction is shown in Figure V-3 for sulfate pulp which had been purified by chlorination and alkali extraction.³² The effect of increased lime is to delay the period of rapid drop in pH and to raise the final pH at the end of the reaction.³² Instead of adding all the required excess alkali at the beginning of the bleaching period, it is possible to add part of the alkali after the bleaching has progressed about halfway.

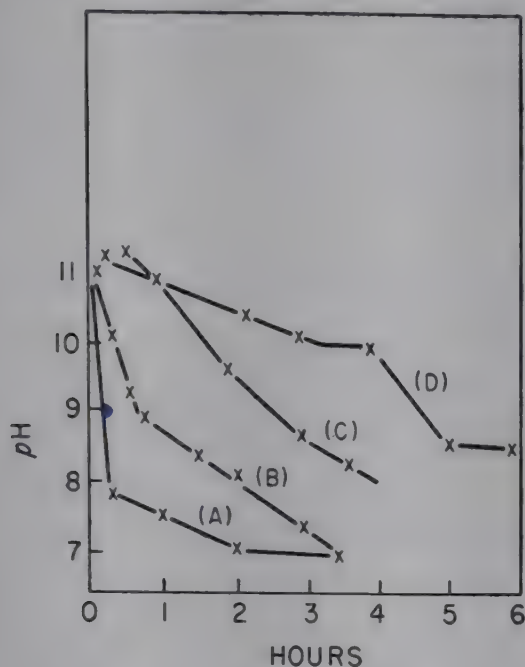


Fig. V-3. Effect of lime on pH during bleaching with hypochlorite. 1.5% available chlorine added as clear hypochlorite saturated with lime. (A) 0, (B) 0.2, (C) 0.4, (D) 0.45 g. lime per gram chlorine.

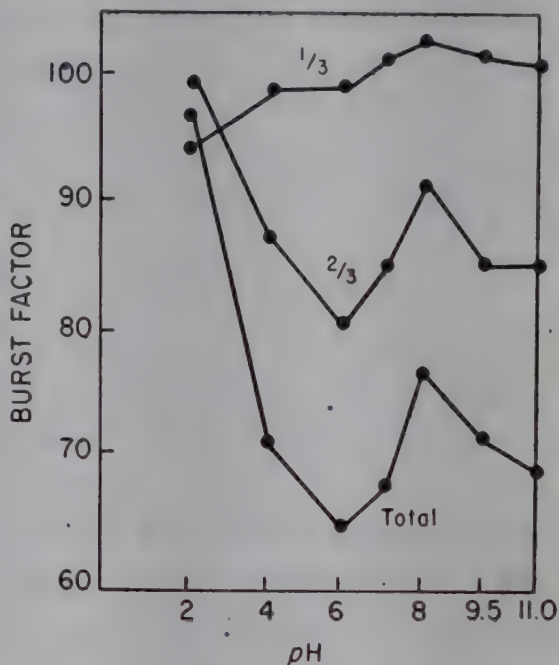


Fig. V-4. Effect of pH of hypochlorite on the bursting strength of sulfate pulp. Consumption of chlorine 1/2, 2/3 and total, as indicated.

This is ideal from the standpoint of maintaining bleaching at a high rate compatible with good strength, but it involves elaborate control of the process. Most commercial bleaching is done with excess lime added at the beginning of the bleaching period to obtain a final pH of 7.0 to 8.0.

For relatively high applications of hypochlorite, the pH should not be too high, i.e., not over 11 at the start and 8 at the finish of the bleaching period, because this results in significant fiber damage, due to the excessively long bleaching period required. Bleaching time increases rapidly if the pH of the reaction mixture at the end of the bleaching period is over about 6.5 to 7.0.^{33, 34} In the case of sulfate pulps, Swartz³⁵ found that

³² J. D. Rue, *The Chemistry of Bleaching Chemical Wood Pulps*, from the *Transactions of the Electrochemical Society* 73 (1938)

³³ F. Casciani and G. K. Storin, *Paper Trade J.* 115, No. 21: 265-269 (Nov. 19, 1942)

burst was highest when the pulp was bleached at a relatively constant pH of 8, as shown in Figure V-4, where the burst factor is plotted against pH at one-third, two-thirds, and complete chlorine consumption. Optimum color, in the case of sulfate pulps, appears to be obtained in a range of 8 to 11 pH .³⁶ Casciani³⁷ recommends a pH level of 7.0 for sulfite pulp and pH level of 7.5 for sulfate pulp.

Sodium silicate, particularly sodium metasilicate, may improve the efficiency of hypochlorite bleaching. Best results are obtained in the case of sulfite and sulfate pulp with about 1% sodium silicate on the basis of the pulp and, in the case of soda pulp, with about 2% sodium silicate on the basis of the pulp.³⁸ The silicate acts to buffer the bleach at the optimum pH for most effective bleaching but Casciani and Storin³⁴ found no advantage in silicate over caustic soda.

Effect of Temperature in Hypochlorite Bleaching

Temperature is second only to pH as a controlling factor in the rate of bleaching with hypochlorite and for the effect of bleaching on the pulp. The rate of chlorine consumption in hypochlorite bleaching is approximately doubled for each 7 to 15° C. rise in temperature. Temperature changes the character of the bleaching reaction by shifting the equilibrium in the chlorine-water system toward an increase in the concentration of hypochlorous acid, hydrogen ion, and chloride ion, and a decrease in the concentration of molecular chlorine, thus increasing the oxidation potential of the system. In other words, the hydrolysis constant for the equation

$$K = \frac{(H^+) (Cl^-) (HOCl)}{Cl_2}$$

TABLE IV

EFFECT OF TEMPERATURE ON HYDROLYSIS CONSTANTS FOR CHLORINE IN WATER

Temp., °C.	K^{38a}	Temp., °C.	K^{39}
0	1.45×10^{-4}	1	1.28×10^{-6}
25	4.84×10^{-4}	15	2.27×10^{-6}
40	7.15×10^{-4}	20	2.44×10^{-6}
60	10.0×10^{-4}	25	3.48×10^{-6}

³⁴ F. Casciani and G. K. Storin, *Paper Trade J.* 115, No. 20: 255-262 (Nov. 12, 1942)

³⁵ J. N. Swartz, *Pulp Paper Mag. Canada* 47: 203-220, Convention Issue (1946)

³⁶ J. N. Swartz, *Pulp Paper Mag. Canada* 47: 203-220, Convention Issue (1946)

³⁷ F. Casciani, *Paper Ind.* 25, No. 4: 427-430 (July, 1943)

³⁸ J. D. Carter, *Ind. Eng. Chem.* 18: 248 (1926)

^{38a} G. N. Lewis and M. Randall, *Thermodynamics*, McGraw-Hill Book Co., New York, p. 508 (1923)

³⁹ R. P. Whitney and J. E. Vivian, *Ind. Eng. Chem.* 33, No. 6: 741-744 (June, 1941)

increases appreciably with temperature, as shown in Table IV, for two different sets of values quoted in the literature. Another effect of high temperature is to cause hypochlorous acid to give up oxygen more readily. High temperature also favors the inward diffusion of oxidizing agent into the regions of the fiber and the outward diffusion of reaction products. Too high a temperature reduces bleaching efficiency by converting part of the hypochlorite to chlorate.

From a practical standpoint, the temperature of bleaching should be as high as possible to speed up the reaction, but not so high that the cellulose is seriously degraded. The optimum temperature depends upon the consistency of the pulp, bleach ratio, and *pH*. In general, about 40° C. is satisfactory,⁴⁰ although temperatures as high as 50° C. are sometimes used commercially. In the bleaching of rag stock with hypochlorite, Crain⁴¹ obtained an approximate linear relation between the loss of viscosity and the temperature of bleaching up to 35° C., and beyond that point, the viscosity decreased even more rapidly. For maximum strength, the bleaching should be carried out at the lowest practical temperature, but optimum brightness appears to be obtained at slightly elevated temperatures. At consistencies of 4 to 6%, bleaching temperatures should not exceed 40° C., at 6 to 10% the temperature should not exceed 38° C., and at 10 to 16% consistency the temperature should not exceed 35° C. In multistage bleaching, temperatures as low as 32° C. are preferred for the last hypochlorite treatment.

To avoid degradation of the cellulose when high bleaching temperatures are used, it is best to heat the stock before the bleach is added in order to avoid local overheating in the presence of bleach. Consideration should be given to the fact that the bleaching reaction itself generates heat and increases the temperature. For 1 g. chlorine consumed, about 1,100 cal. are liberated.⁴² A pulp requiring 5% chlorine may show a temperature rise of about 3° C. when bleached at 5% consistency. In high-density bleaching, there may be an additional increase in temperature as a result of mechanical friction, and the total temperature rise may reach 9 to 10° C.

Effect of Bleach Ratio in Hypochlorite Bleaching

The object in bleaching is to improve the brightness of the pulp without overbleaching. Overbleaching is the point at which a serious loss in strength occurs without a proportionate increase in the brightness of the pulp.

⁴⁰ J. F. White and G. P. Vincent, *Paper Trade J.* 111, No. 12: 159-164 (Sept. 19, 1940)

⁴¹ R. C. Crain, *Paper Trade J.* 103, No. 24: 343-352 (Dec. 10, 1936)

⁴² J. D. Rue, *The Chemistry of Bleaching Chemical Wood Pulps*, from the *Transactions of the Electrochemical Society* 73 (1938)

The correct ratio of bleach liquor to pulp depends upon the bleachability of the pulp, the process by which the pulp is bleached, and the brightness and strength which are desired in the bleached pulp. The bleach requirements of different pulps as measured by single-stage bleaching with hypochlorite are shown in Table V.⁴³ In general, hardwood pulps bleach more readily than softwood pulps, and, as can be seen from Table V, sulfite pulps bleach more easily than sulfate pulps.

Excess bleach of high strength can be added to the pulp and the excess bleach removed as soon as the stock reaches the desired color, or less bleach of lower strength can be added and allowed to exhaust in the stock. The former is a quicker process, but requires careful control to avoid degradation of the cellulose. It necessitates a system to recover the unused bleach or the chemical cost will be high. When excess bleach is added, the rate of

TABLE V

BLEACH REQUIREMENTS OF DIFFERENT PULPS FOR SINGLE-STAGE HYPOCHLORITE

Type of pulp	Bleach requirement, % chlorine as hypochlorite
Easy-bleaching sulfite	3-5%
Average-bleaching sulfite	5-7%
Hard-bleaching sulfite	Up to 10-13%
Hardwood soda pulps	4-6%
Bleachable sulfate	5-8%
Hard-bleaching sulfate	Up to 12-15%

reaction is generally a second order reaction in that it is a linear function of the logarithm of the time of bleaching.

Effect of Consistency (Density) in Hypochlorite Bleaching

Originally, bleaching was done in the beater at low consistencies (3-5%). Later, bleaching at much higher consistencies became increasingly popular because of the increased speed of bleaching and the increased production resulting from the high concentration of bleach to fiber. Other advantages of high-density bleaching are savings in floor space and amount of steam required to heat up the stock. Bleaching units of intermediate consistency were developed by Bellmer (7-9%) and later units were developed by Thorne, Fletcher, Wolf, and others to bleach at consistencies as high as 10 to 25%. At these high consistencies, the stock no longer acts as a fluid. At very high consistencies, the amount of free water is often insufficient to fill the interstices between the fibers.

When bleaching at high consistency, agitators are desirable in the bleachers to obtain uniform mixing of the bleach throughout the stock. In-

⁴³ F. Casciani and A. Heilborn, *Paper Ind.* 17, No. 11: 810-814 (Feb., 1936)

ternal friction due to agitation acts to break up fiber bundles, which is desirable, but too much agitation may induce hydration as a result of the fibers rubbing against each other, and may even damage the fiber. In the Thorne bleacher, mechanical agitation is eliminated during bleaching in that the stock is first mixed with the bleach and then is moved slowly downward in a tower without agitation.

There is a greater chance of overbleaching in high-density systems because of the higher concentration of bleach. High-density bleaching tends to be less uniform than low-density bleaching. More careful control is necessary in high-density bleaching and, as already explained, the temperature of bleaching should be lower than that used in low-density bleaching.

Effect of Hypochlorite on Lignin

It has been mentioned that the major objective of bleaching is to remove or decolorize the lignin left in the pulp from the cooking operation. The amount of lignin in well-cooked pulp is relatively small, but it is enough to give the pulp a poor color. Easy-bleaching sulfite pulp contains less than 3% lignin, whereas a raw kraft cook may contain as much as 8 to 9% lignin, and this must be reduced to less than 1.0 to 1.5% lignin after bleaching. For a given pulp, the bleach demand is closely related to the lignin content, as previously shown. The brightness of the bleached pulp is determined by the residual lignin content, as shown by Giertz,⁴⁴ who found a definite relation between the brightness of bleached pulp and the residual lignin number. The lignin number was determined by dissolving the pulp in 76% sulfuric acid and measuring the color of the solution in a colorimeter.

Lignin is subject to both oxidation and chlorination. Either of these reactions can occur in hypochlorite bleaching, depending upon the pH . At the high pH values normally used in hypochlorite bleaching, the reaction is considered to be primarily an oxidation of the lignin.

Forni⁴⁵ found that the removal of lignin in the bleaching of a sulfite spruce pulp does not take place until 20% of the bleach requirement of the pulp has been satisfied, but that lignin is then removed rapidly to 70% of the bleach requirement. In the early stages of hypochlorite bleaching, the bleachability (as evidenced by the permanganate number) decreases rapidly, although the lignin content is not appreciably reduced.⁴⁶ Apparently, in the early stages, the lignin is changed chemically, which accounts for the lowering of the permanganate number, but the lignin is not appreciably re-

⁴⁴ H. W. Giertz, *Svensk Papperstidn.* 48, No. 20: 485-489 (Oct. 31, 1945)

⁴⁵ P. A. Forni, *Paper Trade J.* 119, No. 11: 108-112 (Sept. 14, 1944)

⁴⁶ P. A. Forni, *Paper Trade J.* 119, No. 11: 108-112 (Sept. 14, 1944)

moved until about 20% of the bleach demand has been satisfied. Then, the lignin begins to dissolve and the permanganate number decreases with a decrease in lignin content in a straight-line function. The results in Table VI, which shows the relationship between bleach demand, permanganate number, and lignin removal, were taken from work by Forni.⁴⁷ A spruce sulfite pulp was used which had a permanganate number of 8.8 and a bleach requirement of approximately 82.8 lb. of chlorine (as calcium hypochlorite) per ton. The bleach demand (100%) was taken as 80 lb. chlorine per ton of pulp.

TABLE VI

EFFECT OF BLEACHING WITH HYPOCHLORITE ON LIGNIN CONTENT, BRIGHTNESS, AND PERMANGANATE NUMBER OF SPRUCE SULFITE PULP WITH PERMANGANATE NUMBER 8.8

Bleach demand, %	Brightness	Lignin content, %	Permanganate number
0	57.9	1.96	8.80
10	52.8	1.95	7.09
20	54.2	1.85	5.95
30	57.8	1.51	4.95
50	67.7	0.82	3.50
70	72.9	0.50	1.60
90	79.0	...	1.40
110	81.4	...	1.20

The ease with which lignin can be removed with hypochlorite depends upon the species of wood, type of cooking process, and degree of cooking. Sulfite pulps are easier to bleach with hypochlorite than sulfate pulps because the lignin residues in sulfite pulp are partially sulfonated and consequently are more readily solubilized with hypochlorite. Sulfate and soda pulps produced from softwoods cannot be satisfactorily bleached with single-stage hypochlorite. Hardwood soda pulps can, however, be bleached with hypochlorite in a single stage.

Treating pulp with ultraviolet light at wavelength 360–385 millimicrons is said to activate lignin so that its reaction with bleach liquor is accelerated, while the cellulose is not affected.⁴⁸

Effect of Hypochlorite on Coloring Matter

Until recently, it was believed that lignin was solely responsible for the dark color of unbleached pulps. Lignin is undoubtedly an important contributing factor, but it is now believed that other substances, whose chemical

⁴⁷ P. A. Forni, *Paper Trade J.* 119, No. 11: 108–112 (Sept. 14, 1944)

⁴⁸ W. Hirschkind, D. J. Pye and E. G. Thompson, *Paper Trade J.* 105, No. 18: 268–269 (Oct. 28, 1937)

structure is as yet unknown, are responsible to a large degree for the dark color of unbleached pulps. These substances are believed to be responsible for the consumption of large amounts of chlorine in the bleaching process and account for the difficulty in bleaching certain pulps to a high degree of permanent whiteness. Coloring substances are particularly noticeable in sulfate pulps obtained from southern pines and are partly responsible for the difficulty of color removal in these pulps.

Freshly made sulfate pulp has a light brown, grayish color, but upon contact with air, it becomes oxidized to a dark brown color which is difficult to decolorize. The coloring agents acts as an indicator, since the pulp becomes lighter in color in acid solution and returns to a dark brown color in alkaline solution. A temporary darkening generally occurs upon the addition of hypochlorite.

The agents responsible for color in unbleached pulps have been described as degraded lignin products, phlobatannins,⁴⁹ reaction products of lignin and iron, reaction products of cellulose and iron, flavones, resinous residues from soaps formed during the cooking process,⁵⁰ sulfur dyes, and other various substances. Bard⁵¹ believes that colored substances are formed through a combination of the tannins with degraded products of the non-resistant carbohydrates, perhaps by the familiar phenolaldehyde type of condensation. Tannin by itself has little effect on the color. Hibbert and coworkers⁵² believe that natural phlobatannins are not the source of color, but that the coloring matter is due to the degraded lignin products formed during the alkaline cooking process.

Effect of Hypochlorite on Carbohydrates

The object of bleaching is to destroy and remove the coloring matter in the pulp without affecting the carbohydrate fraction. There is, however, in hypochlorite bleaching some attack on the carbohydrates. The extent of this attack depends upon the time of bleaching, temperature of bleaching, pH, density, and bleach ratio, as previously shown. The amount of carbohydrate removal depends upon the severity of bleaching which, in turn, is dependent upon the amount of lignin in the pulp.⁵³ However, loss of yield is never large, being about 2 to 3% for easy-bleaching pulps and 7 to 8% for hard-bleaching pulps, not including mechanical losses, and most of this loss in yield is due to lignin removed.

The attack on cellulose during bleaching with chlorine is manifested by a

⁴⁹ W. F. Holzer, *Paper Trade J.* 99, No. 12: 91-103 (Sept. 20, 1934)

⁵⁰ M. L. Griffin, *Paper Trade J.* 78, No. 15: 174 (1924)

⁵¹ J. W. Bard, *Paper Trade J.* 113, No. 12: 137-142 (Sept. 18, 1941)

⁵² H. Schwartz, J. L. McCarthy and H. Hibbert, *Paper Trade J.* 111, No. 18: 230-234 (Oct. 31, 1940)

⁵³ L. L. Larson, *Paper Trade J.* 113, No. 21: 263-269 (Nov. 20, 1941)

reduction in the viscosity and alpha cellulose content of the pulp, illustrated by the results shown in Table VII, for the bleaching of sulfite pulp with chlorine at two different pH values.⁵⁴ Increases in the copper number and the hot alkali solubility are other evidences of attack on the cellulose when bleaching with chlorine (see Table VII). Forni⁵⁵ found that the alpha cellulose content decreases at a uniform but slow rate until the pulp is bleached to 100% of the bleach requirement, after which further bleaching causes a rapid decrease in alpha cellulose. The cellulose is more susceptible to attack in the later stages of bleaching because the impurities have been removed and the internal surface of the fibers has been increased, with the

TABLE VII

EFFECT OF BLEACHING WITH CHLORINE ON PROPERTIES OF SULFITE PULP
Active chlorine added, 2%; temperature, 40° C.; consistency, 6%

Bleaching time, min.	pH	Active chlorine consumed, %	TAPPI viscosity (T206), cp.	Alpha cellulose content, %	Hot alkali (7%) solubility, %	Copper number, g. Cu/100 g. pulp
0	29.6	89.7	29.0	1.98
10	3.0	0.82	16.2	87.3	30.9	2.66
30	3.0	0.94	13.3	84.8	34.5	2.92
60	3.0	1.26	9.9	80.6	39.4	4.81
180	3.1	1.93	6.3	70.9	50.0	7.87
420	3.0	2.00	6.4	71.3	53.0	7.76
5	8.5	0.73	24.8	89.3	27.0	2.12
15	8.7	0.75	24.4	89.4	25.6	1.92
45	8.7	0.83	19.5	89.1	24.5	1.70
90	8.5	0.90	15.1	87.2	26.6	2.02
180	8.6	1.18	12.6	86.5	27.4	2.25
360	8.6	1.55	7.9	79.4	35.3	3.03

result that the cellulose is in a more reactive state. However, the sudden reduction in alpha cellulose content toward the end of the bleaching period can be attributed in part to the characteristic sharp decrease in alpha cellulose which occurs when the viscosity drops below a critical value.

It is possible in multistage bleaching to bleach with hypochlorite without appreciable loss in alpha cellulose,⁵⁶ but singlestage bleaching usually results in appreciable decrease in alpha cellulose content. However, if the conditions of bleaching are not carefully controlled, there will be considerable oxidation of the cellulose and an appreciable loss in fiber

⁵⁴ O. Samuelson and C. Ramsel, *Svensk Papperstidn.* 53, No. 6: 155-163 (March 31, 1950)

⁵⁵ P. A. Forni, *Paper Trade J.* 119, No. 11: 108-112 (Sept. 14, 1944)

⁵⁶ F. Casciani and G. K. Storin, *Paper Trade J.* 115, No. 14: 163-171 (Oct. 1, 1942)

strength.⁵⁷ Cotton pulp is less susceptible than wood pulp. There is generally some shifting in the proportion of alpha, beta, and gamma cellulose in the pulp. Overbleaching increases the amount of degraded celluloses: for example, in one case the alpha cellulose content was reduced from 88 to 85%, while the beta cellulose was increased from 4 to 8%.⁵⁸ On the other hand, it is possible to produce pulp of very high alpha cellulose content by bleaching at a subdued rate of reaction using strongly alkaline bleach so that the low molecular weight carbohydrates are removed from the pulp, but the main cellulose fraction is not degraded.⁵⁹

Effect of Hypochlorite on Pulp (Sheet-Forming) Strength

Overbleaching reduces fiber strength by forming oxycellulose and hydrocellulose, which are weaker than the original cellulose. Even under mild bleaching conditions, there is probably some loss in individual fiber strength. In addition to the loss in individual fiber strength, commercial bleaching with hypochlorite is generally associated with some loss in pulp (sheet-forming) strength. Alkaline cooked pulps almost always lose strength when bleached with hypochlorite, and generally sulfite pulps lose some strength.

Bleaching may accelerate the rate of beating of pulp in water.⁶⁰ Baird and Doughty⁶¹ found that bleaching of spruce sulfite pulp reduced the milling time required for the development of maximum strength in a laboratory ball mill from 100 to 60 minutes. Musser and Engel⁶² report that the beating of cotton pulp was accelerated by a reduction in the viscosity of the pulp brought about by the use of bleaching agents. Overbleaching of commercial rag pulps at elevated temperatures makes the pulp beat more easily, although the ultimate fiber strength is decreased. Along the same line, Greenwood⁶³ noted that bleaching increased the cohesion of cotton fibers in yarn, even though it decreased the tensile strength of the individual fibers.

When carried out under controlled conditions, bleaching may increase the strength of the paper made from the pulp.⁶⁴ Bleaching of a raw wood pulp tends to increase bursting strength (unless the fibers are degraded by overbleaching) because of the removal of encrustants which increases the

⁵⁷ H. Staudinger and I. Jurisch, *Papier-Fabr.* 35, No. 49: 459-462 (Dec. 3, 1937)

⁵⁸ N. W. Coster and R. Vincent, *Paper Trade J.* 119, No. 12: 117-119 Sept. 21, 1944)

⁵⁹ J. Frankevicz and N. I. Bearce, *Paper Trade J.* 113, No. 8: 83-86 (Aug. 21, 1941)

⁶⁰ C. G. Schwalbe, *Papier-Fabr.* 25: 481 (1927)

⁶¹ P. K. Baird and R. H. Doughty, *Paper Trade J.* 90, No. 9: 97-101 (Feb. 20, 1930)

⁶² D. M. Musser and H. C. Engel, *Paper Trade J.* 114, No. 15: 173-175 (Apr. 9, 1942)

⁶³ R. S. Greenwood, *J. Text. Inst.* 10, 274-278 (1919)

⁶⁴ G. Porrvik, *Svensk Papperstidn.* 30: 40-44 (1927) through *A. C.* 21, p. 2062

fiber surface available for bonding. Forni⁶⁵ noted that the tearing strength was greater after bleaching than before bleaching. Parsons⁶⁶ noted that the bursting strength and folding endurance increased to a maximum value which corresponded closely to the completely bleached pulp, but that beyond that point, a decline in strength took place, due to degradation of the fiber. Swanson and Monsson⁶⁷ conclude that a properly cooked sulfite pulp does not lose strength when properly bleached, but that overbleaching quickly lowers the strength. Swartz⁶⁸ found that the burst factor of partly bleached pulp increased above the original value of the unbleached pulp at a one-third consumption of chlorine, although the burst decreased when two-thirds or more of the chlorine was consumed. Casciani and Storin⁶⁹ found, in the single-stage hypochlorite bleaching of sulfite pulp, that the strength properties of the pulp were not appreciably affected until a brightness of 74 was reached, after which the burst and tear tests dropped materially and the pulp hydrated more readily. Baird and Doughty⁷⁰ obtained no loss in bursting strength when easy bleaching sulfite pulp was treated with 12 to 17% bleach, although the fold and tearing strengths were slightly decreased. It should be noted that the strength increases obtained on bleaching generally occur only with sulfite pulps, but do not occur in the bleaching of alkaline cooked pulps (soda and sulfate) because of the more severe bleaching conditions required with the latter. However, highly lignified pulps generally show an initial increase on bleaching, followed by a decrease.

It is obvious from the above that overbleaching not only decreases the strength of the individual fibers, but also reduces the strength of the paper made from the fibers. The degradative effects of overbleaching can be measured by the copper number, although it is possible for a significant loss in pulp strength to occur before the copper number shows a significant increase.⁷¹ The cuprammonium viscosity test is better suited for measuring degradation, since it gives greater numerical differences than the copper number. Generally, reduced cuprammonium viscosity is apparent before there is any serious impairment of the physical properties of paper made from a given pulp,⁷² but a large change in viscosity is always accompanied

⁶⁵ P. A. Forni, *Paper Trade J.* 119, No. 11: 108-112 (Sept. 14, 1944)

⁶⁶ J. L. Parsons, *Paper Trade J.* 93, No. 1: 42-44 (July 2, 1931)

⁶⁷ W. H. Swanson and W. H. Monsson, *Paper Trade J.* 82, No. 4: 62-64 (Mar. 4, 1926)

⁶⁸ J. N. Swartz, *Pulp Paper Mag. Canada* 47: 203-220, Convention Issue (1946)

⁶⁹ F. Casciani and G. K. Storin, *Paper Trade J.* 115, No. 20: 255-262 (Nov. 12, 1942)

⁷⁰ P. K. Baird and R. H. Doughty, *Paper Trade J.* 90, No. 9: 97-101 (Feb. 20, 1930)

⁷¹ J. L. Parsons, *Paper Trade J.* 93, No. 1: 42-44 (July 2, 1931)

⁷² J. L. Parsons, *Paper Trade J.* 93, No. 1: 42-44 (July 2, 1931)

by a decided alteration in the physical properties of the paper.⁷³ Klauditz⁷⁴ noted that the strength is retained as long as the viscosity is not lowered below about 30 (polymerization value of about 900). Crain⁷⁵ has also shown that there is no appreciable drop in tear and bursting strength of paper made from bleached rag stock until the cuprammonium viscosity drops below 30 to 40 cp., after which the strength values begin to decrease rather rapidly. According to Musser and Engel,⁷⁶ oxidizing agents have less harmful effect on the physical properties of paper than acids for a comparable reduction in viscosity.

Kress and Brainerd⁷⁷ found that overbleaching tends to embrittle the fiber so that it is less able to resist the cutting action of the beater or jordan. This results in fiber fragmentation upon beating and an accompanying loss in tensile strength of the fiber. The ability of a bleached pulp to resist this cutting action is related to the alpha cellulose content and copper number of the pulp. Because of the more fragile nature of bleached pulps, it is best, when using mixed furnishes of bleached and unbleached pulps, to furnish the bleached pulp after the unbleached has been partially beaten.

Effect of Hypochlorite on Brightness

As mentioned previously, bleaching of papermaking grades of pulp is designed to remove the coloring matter in the pulp and produce, as nearly as possible, a pure white pulp without lowering the physical and chemical properties of the pulp beyond a practical limit. Bleaching is therefore a compromise between a treatment which produces a pure white pulp and a treatment which retains the maximum potential strength of the fibers. The brightness test is generally used for measuring the reflectance of bleached pulps (see Ch. XVI).

The rate of color improvement in hypochlorite bleaching does not coincide with the rate of chlorine consumption. In hypochlorite bleaching, the brightness value passes through a minimum just before the bleach begins to brighten the stock,⁷⁸ as shown in Figure V-5 for a spruce sulfite pulp. Likewise, Toovey⁷⁹ found that sulfite pulps bleached with 40 to 50% or less of the theoretical requirement have a color lower than that of the unbleached pulp. This initial dark color at low chlorine consumption is presumably due to the formation of colored, chlorinated compounds. Soon after the initial decrease in color, the brightness begins to increase practically as a

⁷³ G. H. McGregor, *Paper Trade J.* 102, No. 11: 155-167 (Mar. 12, 1936)

⁷⁴ W. Klauditz, *Papier-Fabr.* 38: 223-227 (Oct. 4, 1940)

⁷⁵ R. C. Crain, *Paper Trade J.* 103, No. 24: 343-352 (Dec. 10, 1936)

⁷⁶ D. M. Musser and H. C. Engel, *Paper Trade J.* 114, No. 15: 173-175 (Apr. 9, 1942)

⁷⁷ O. Kress and F. W. Brainerd, *Paper Trade J.* 98, No. 13: 35-39 (Mar. 29, 1934)

⁷⁸ P. A. Forni, *Paper Trade J.* 119, No. 11: 108-112 (Sept. 14, 1944)

⁷⁹ T. W. Toovey, *Paper Trade J.* 114, No. 7: 65-68 (Feb. 12, 1942)

linear function of bleach liquor consumption. This increase continues up to a second point, after which only a slight increase in brightness takes place at the expense of relatively large amounts of bleach. Obviously, the bleaching reaction should be stopped at the second break in the brightness curve.

One of the undesirable aftereffects of bleaching with hypochlorite is color reversion, or a loss in brightness of the pulp. This occurs more often with some pulps than with others and depends a great deal upon the conditions of bleaching. Sulfate pulps are, as a rule, more susceptible than sulfite pulps, but today, well-bleached and well-washed sulfate and sulfite pulps have little tendency toward color reversion if they are not subjected to excessive heat, air, or light after bleaching. However, this is not true of single-stage bleached pulps.

Either overbleaching or underbleaching can be responsible for the yellowing of pulp on aging. Underbleaching leads to reversion because of

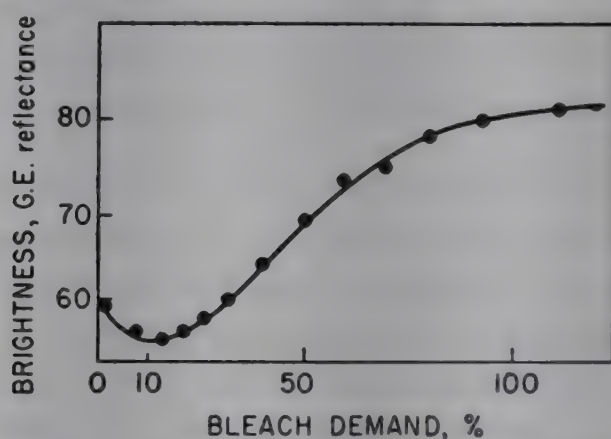


Fig. V-5. Effect of hypochlorite on brightness of spruce sulfite pulp.

failure to remove the matter most subject to color reversion. Overbleaching results in a degradation of the cellulose, thereby making it more susceptible to color change. Giertz⁸⁰ lists decomposed carbohydrates, rather than lignin or resins, as the chief cause of discoloration of bleached pulps in accelerated aging. He found yellowing to be greatest in strong sulfite pulp, less in soft sulfite pulp, and practically non-existent in carefully bleached sulfate pulp.

It is normally considered good practice to maintain at least a small residual of active chlorine up to the time that washing is begun in order to avoid the possibility of color reversion. Bleaching to a low final pH value in the case of hypochlorite appears to increase the resistance to color fading.^{81,82} Acid souring with dilute sulfurous acid at the end of the bleaching period is also said to help prevent color reversion.

⁸⁰ H. W. Giertz, *Svensk Papperstidn.* 48, No. 13: 317-323 (July 15, 1945)

⁸¹ F. Casciani and G. K. Storin, *Paper Trade J.* 115, No. 21: 265-269 (Nov. 19, 1942)

⁸² F. Casciani and G. K. Storin, *Paper Trade J.* 115, No. 20: 255-262 (Nov. 12, 1942)

Perhaps the biggest factor in the prevention of color reversion is the washing of the pulp to remove all the reaction products of bleaching. According to Prelinger,⁸³ the permanency of color of bleached pulps is directly related to the amount of soluble oxidizable material left in the pulp. Good washing is particularly important in the case of sulfate pulps, since most of the encrustants in sulfate pulp are located deep within the fiber. Poorly washed pulp will revert in color on standing in wet lap form because of diffusion of soluble coloring matter to the surface of the wet lap. A similar effect may take place during the drying of paper made from poorly washed pulp.⁸⁴

Purification of Pulp by Chlorination

The principle of using chlorine directly as a delignifying agent is an old idea, but it has not been used extensively until modern times because of the lack of suitable equipment for handling the corrosive gas. Chlorination of pulp is now an established part of most bleaching processes, although strictly speaking, it is a pulp purification process, rather than a true bleaching process.

Chlorination is never used by itself, but instead is used in conjunction with hypochlorite and special washing treatments in multistage bleaching. Purifying by chlorination is well suited to sulfite, soda, and sulfate pulps. It has made possible the multistage bleaching of sulfate pulps which are difficult to bleach with single-stage hypochlorite. Chlorination will be described first by itself and discussed again later in relation to multistage bleaching.

Application of Chlorine in Direct Chlorination

In direct chlorination, the chlorine is added directly to the pulp, either as the chlorine gas or as a chlorine-water solution. Chlorine is not very soluble in water, as shown in Table VIII,⁸⁵ but in the presence of pulp, chlorine is absorbed readily. The chlorine should be added rapidly in order to lower the *pH* of the reaction mixture as quickly as possible. The reason for this, as previously mentioned, is to establish the desired composition of the chlorine-water system.

Chlorine is received at the paper mill in liquid form in any one of three different ways: in 100- or 150-lb. cylinders, 1-ton tank car cylinders, or in full-sized tank cars of 16-, 30-, or 55-ton capacity. The small cylinders are equipped with only one valve for drawing off gas (or liquid if turned upside down), but the 1-ton cylinders and tank cars are equipped for drawing

⁸³ H. Prelinger, *Paper Trade J.* 107, No. 11: 121-126 (Sept. 15, 1938)

⁸⁴ C. S. Hamm, *Paper Trade J.* 76, No. 16: 142-143 (Apr. 19, 1923)

⁸⁵ R. P. Whitney and J. E. Vivian, *Ind. Eng. Chem.* 33, No. 6: 741-744 (June, 1941)

off either gaseous or liquid chlorine. In the case of tank cars, the chlorine is usually withdrawn as a liquid, and then if gas is desired, the chlorine is allowed to vaporize in a vaporizer. Gas is not drawn directly because of the cooling effect of evaporation which lowers the temperature of the chlorine in the tank, thereby reducing its vapor pressure to the point where the flow of gas is reduced.

Chlorine may be weighed or metered into the stock or added unmetered to maintain a definite chlorine residual. The operation may be carried out either in a batch or in a continuous process, but the chlorine should be introduced into the stock at or near the point of maximum turbulence to insure its even blending and absorption by the pulp. One process calls for adding

TABLE VIII

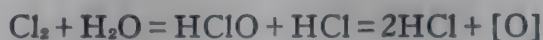
SOLUBILITY OF CHLORINE IN WATER AT DIFFERENT TEMPERATURES

Temperature, °C.	Solubility, g./100 g. water
10	0.992
15	0.846
20	0.732
25	0.633

the chlorine while the pulp is flowing through a special spiral piping system. Because the stock is in a state of turbulence, a very uniform mixture is obtained.

Reaction of Chlorine with Lignin

Three principal reactions occur in the chlorination of wood pulp, viz.: substitution, addition, and oxidation. Substitution involves the replacement of hydrogen atoms in the lignin molecule with chlorine, thereby forming one molecule of hydrochloric acid as a by-product for each molecule of chlorine substituted. Addition involves the reaction of chlorine with lignin at the unsaturated double or triple bonds, thereby forming no by-product. Oxidation involves the reaction of nascent oxygen with the lignin, forming two molecules of hydrochloric acid per molecule of chlorine consumed. The oxidation reaction can be expressed as follows:



Ordinarily, from 50 to 75% of the chlorine applied in the chlorination of pulp appears as hydrochloric acid,^{86,87} the rest being combined with the solubilized material or reacted with the residual lignin in the pulp to form chlorolignins. The large amount of hydrochloric acid formed indicates that

⁸⁶ H. Heiwinkel and E. Hägglund, *Svensk Papperstidn.* 43: 391-397 (Nov. 15, 1940)

⁸⁷ F. Kraft, *Papier-Fabr.* 36: 429-436 (Oct. 14, 1938)

substitution and oxidation are the predominant reactions. The chlorine combined with the chlorolignins tends to split off when the chlorolignins are dissolved in alkali.

It has been concluded from a study of reaction rates that two separate and distinct reactions occur upon chlorination.^{88, 89} Hibbert and coworkers⁹⁰ state that the reactions are an initial rapid reaction involving partial demethoxylation and chlorination, and a second slow reaction involving oxidation. Hatch⁹¹ believes that the actual chlorination of sulfite pulp is practically complete at about 40% of the bleach demand, which is the point where the curve of residual bleachability versus percentage addition of total bleach demand shows a sharp break. Beyond that point, the slower oxidation reaction is believed to predominate.

In the chlorination reaction, Hibbert and coworkers believe that chlorine enters the lignin molecule ortho to a methoxyl group, thereby resulting in a simultaneous cleavage of the methoxyl group. The greater the degree

TABLE IX
CHLORINE CONSUMPTION OF SULFITE PULPS

	Pulp A		Pulp B	
Lignin content, % of pulp	3.85	3.85	15.2	15.2
Chlorine added, % of total chlorine demand	35	75	35	75
Chlorine consumed on basis of total reactants, %	2.0	4.2	6.4	12.8
Chlorine consumed on basis of lignin, %	54	114	45	96

of chlorination the greater the loss of methoxyl.^{92, 93} The entrance of chlorine into the lignin molecule increases the solubility of the lignin, causing the lignin to pass into solution. The lignins dissolved in chlorination are low in methoxyl content and rich in chlorine.⁹⁴ According to calculations by Carmody and Mears,⁹⁵ sixteen chlorine atoms react with each lignin building unit of 870, or a ratio of about 40% chlorine. Results obtained by Larson in Table IX⁹⁶ show that the amount of chlorine consumed

⁸⁸ W. R. Carmody and J. S. Mears, *Paper Trade J.* 106, No. 20: 38-40 (May 19, 1938)

⁸⁹ E. V. White, J. N. Swartz, Q. P. Peniston, H. Schwartz, J. L. McCarthy and H. Hibbert, *Paper Trade J.* 113, No. 24: 299-309 (Dec. 11, 1941)

⁹⁰ E. V. White, J. N. Swartz, Q. P. Peniston, H. Schwartz, J. L. McCarthy and H. Hibbert, *Paper Trade J.* 113, No. 24: 299-309 (Dec. 11, 1941)

⁹¹ E. Ott, ed., *Cellulose and Cellulose Derivatives*, Interscience Publishers, Inc., New York, pp. 577-578 (1943)

⁹² L. L. Larson, *Paper Trade J.* 113, No. 21: 263-269 (Nov. 20, 1941)

⁹³ E. V. White, J. N. Swartz, Q. P. Peniston, H. Schwartz, J. L. McCarthy and H. Hibbert, *Paper Trade J.* 113, No. 24: 299-309 (Dec. 11, 1941)

⁹⁴ H. F. Lewis, *Tech. Assoc. Papers* 25: 436-440 (1942)

⁹⁵ W. R. Carmody and J. S. Mears, *Paper Trade J.* 106, No. 20: 292-294 (May 19, 1938)

⁹⁶ L. L. Larson, *Paper Trade J.* 113, No. 21: 263-269 (Nov. 20, 1941)

by lignin in chlorination depends upon the percentage of the total chlorine demand added as chlorine.

In the case of sulfate pulps, it is not practical commercially to chlorinate to the point of complete water solubility, since this is wasteful of chlorine. The accepted practice is to chlorinate the lignin partially and then remove the chlorolignins by dissolving in alkali. Certain of the chlorinated residues in sulfate pulp are insoluble in dilute alkali so that it is customary to use another stage involving hypochlorite for removing these residues. The subject of multistage bleaching is discussed in the following section. Figure V-6 shows the relationship between the per cent bleachable materials removed, brightness obtained, and total chlorine consumed to the amount of chlorine added in the chlorination of sulfite and sulfate pulps.^{96a}

Effect of Chlorine on Carbohydrates

As a rule, the reaction between chlorine and lignin is much more specific than the reaction between hypochlorite and lignin. Under ordinary conditions, practically no carbohydrate material is removed in chlorination of a normal pulp, although in the case of raw pulps, some carbohydrate material may be removed.⁹⁷

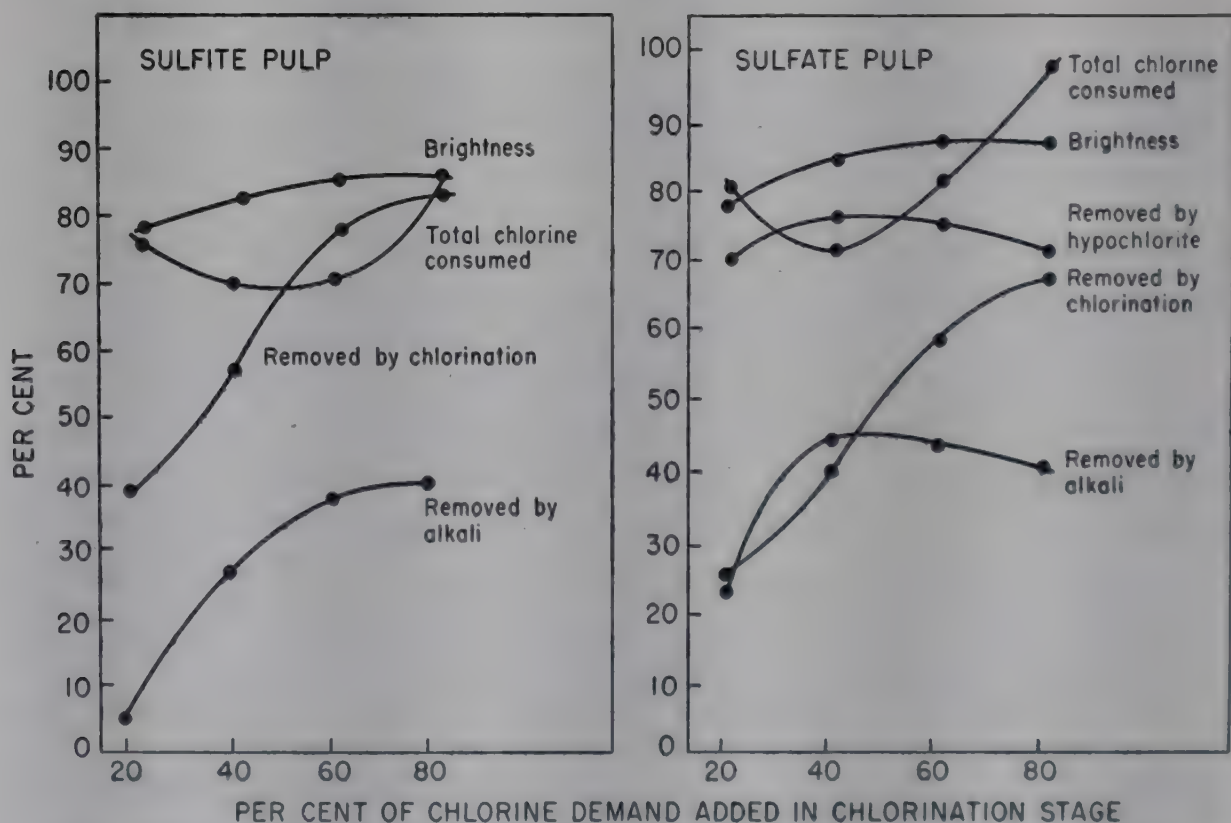


Fig. V-6. Relationship between per cent bleachable materials removed, brightness attained, and total chlorine consumed to the amount of chlorine added in the chlorination stage for sulfite and sulfate pulps.

^{96a} O. S. Sprout and T. W. Toovey, *Paper Trade J.* 124, No. 11: 107-116 (Mar. 13, 1947)

⁹⁷ L. L. Larson, *Paper Trade J.* 113, No. 21: 263-269 (Nov. 20, 1941)

For a given average commercial pulp, chlorination generally results in a smaller decrease in the cuprammonium viscosity of the pulp than hypochlorite bleaching. After a slight initial drop in viscosity, there is generally no further decrease. Even an excess of chlorine over that required for solubilization of the lignin can be used without serious degradation of the fibers, because under ordinary conditions, chlorine reacts with the lignin in the pulp and leaves the cellulose relatively unaffected. Hydrochloric acid is formed as a by-product of chlorination, but the amount of this acid is not sufficient to harm the cellulose under normal conditions. In certain cases, pulp strength is actually increased by chlorination, because of the removal of encrustants which interfere with fiber bonding.

Variables in Chlorination

The fact is well established that chlorination is initially very fast (up to about 90% consumption) and then slows down considerably in the later

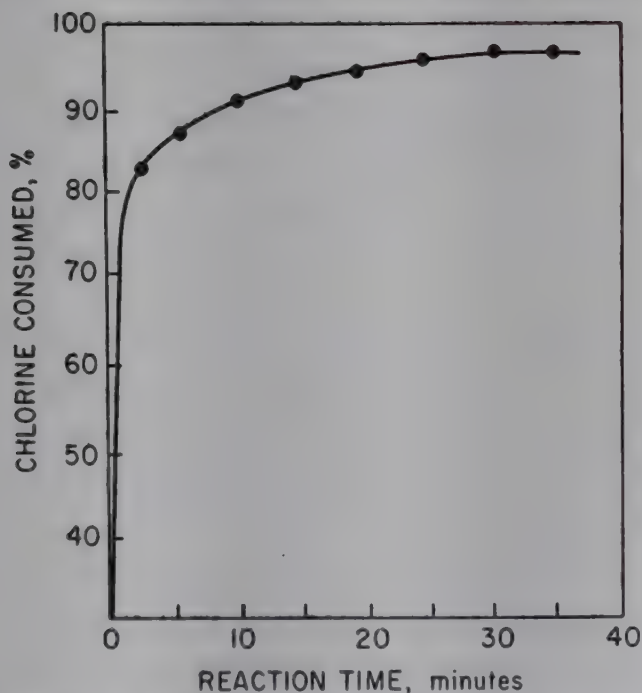


Fig. V-7. Effect of time on the consumption of chlorine by sulfite pulp, pulp treated with 60% of its chlorine demand.

stages of the reaction. Sprout and Toovey⁹⁸ found that approximately 85 to 90% of the chlorine is absorbed within 5 minutes when sulfate pulp is treated with 60% of its chlorine demand (5.22% chlorine) in the chlorination stage, as shown in Figure V-7. It is likely that the chlorination of lignin is almost an instantaneous reaction, and that the time necessary in chlorination is required for the diffusion of chlorine to the secondary wall lignin. Chlorination practically ceases at the end of 30 to 45 minutes.⁹⁹

⁹⁸ O. S. Sprout and T. W. Toovey, *Paper Trade J.* 124, No. 11: 107-116 (Mar. 13, 1947)

⁹⁹ H. W. Giertz, *Svensk Papperstidn.* 46, No. 7: 152-161 (Apr. 15, 1943)

Exhaustion of chlorine in the chlorination stage of commercial bleaching is generally carried to about 90 to 95%.

Chlorination of lignin takes place to some extent over the entire pH range,¹⁰⁰ but as might be expected, the rate is greatly increased at low pH values. Chlorine-water solutions have a pH in the neighborhood of 2, but the pH drops to a lower value in the presence of the pulp, due to hydrochloric acid formed as a result of chlorination. The pH of the stock during chlorination should be kept in the neighborhood of 1.6 to 1.7. If the pH gets much higher than this, there is danger of excessive attack on the cellulose, due to an increase in the concentration of hypochlorous acid. A substantial amount of hypochlorous acid is present even at pH values as low as 1.0, and this becomes great enough to attack the cellulose at somewhat higher pH values (see Table II).

The amount of chlorine used in chlorination is not as critical as that used in hypochlorite bleaching, since lignin will take up large quantities of chlorine (for example, spruce lignin will take up as much as 30 to 40% chlorine). However, if too much chlorine is added to pulp, the excess is not consumed in a typical chlorination reaction. The use of excess chlorine has two bad effects: (1) it results in unnecessary reaction between the chlorine and the already chlorinated lignins; (2) it results in some oxidative attack on the cellulose, thus decreasing the alpha cellulose content of the fibers.

Over an appreciable part of the temperature range, the consumption of chlorine bears a linear relationship to the temperature.¹⁰¹ However, close control of temperature is not as important in chlorination as it is in hypochlorite bleaching. Sulfite pulps react readily with chlorine, even at 0° C. Sulfate pulps react slowly with the amount of chlorine generally used unless the temperature is 15–25° C. If the temperature is too high, there is a tendency for chlorine to be transformed into hypochlorous acid, thereby favoring oxidation at the expense of chlorination. Kress and Voigtman¹⁰² found that temperatures over 20° C. increased the hypochlorous acid sufficiently to cause degradation of spruce Mitscherlich pulp.

Multistage Bleaching with Chlorine Compounds

One of the important commercial developments in pulp purification is multistage bleaching. Multistage bleaching is a method of pulp purification whereby the purifying and bleaching chemicals are added in stages, sepa-

¹⁰⁰ F. Loeschbrandt, *Bleaching of Sulfate Pulp*, translated by E. Martin, reprinted by TAPPI (1941)

¹⁰¹ F. Loeschbrandt, *Bleaching of Sulfate Pulp*, translated by E. Martin, reprinted by TAPPI (1941)

¹⁰² O. Kress and E. H. Voigtman, *Paper Trade J.* 97, No. 7: 73–88 (Aug. 17, 1933)

rated by intermediate washing stages with water or alkali, in which the reaction products are removed. In multistage bleaching, the various impurities in the fiber are removed in a gradual and orderly way without serious degradation of the fiber in any one stage.

In single-stage bleaching, the coloring matter and lignin become soluble after their color is completely destroyed. Multistage bleaching makes use of this fact by adding the bleach in stages so that the soluble reaction products formed in the first stage can be removed by washing before the remaining bleach is added in the second stage. Bleaching this way is more efficient because the solubilized materials are removed before they can take up additional chlorine in side reactions. Thus, the bleach demand of the pulp is lowered.

In the early days of multistage bleaching, hypochlorite was used in two stages, which resulted in a saving of about 15% in chlorine and lime and a slight improvement in the color and quality of the pulp. Since then, it has been found more advantageous to use different purification and bleaching agents in the separate stages in order to take advantage of their different actions on the pulp. In modern multistage bleaching, there is at least one stage involving direct chlorination and another stage involving the use of alkaline hypochlorite.

Modern multistage bleaching has made possible savings in chlorine of 10% or less for easy bleaching pulps to as high as 50% for pulps of high lignin content. Furthermore, multistage bleaching has made it possible to produce strong white papers from sulfate pulps which could not be bleached satisfactorily with straight hypochlorite. The advantages of multistage bleaching with direct chlorine and hypochlorite over conventional single-stage bleaching with hypochlorite may be summed up as follows: (1) saving in chlorine, (2) saving in lime, (3) improvement in tearing and bursting strength, (4) lower ash content of the pulp, (5) higher alpha cellulose content of the pulp, and (6) less color reversion in the bleached pulp. Pulps bleached by multistage bleaching generally require longer beating time than single-stage bleached pulps.

Batch versus Continuous Bleaching

Multistage bleaching may be done in either a batch or a continuous process. Batch processes are widely used, but the trend is toward continuous flow.

In continuous bleaching, chlorination is usually carried out at low density in chlorination towers of the Thorne or Kamyr types. In the Thorne system, the chlorine is mixed with the pulp in a special mixing device and then passed downward through a reaction tower. In the Kamyr system, a circulation pump is placed at the bottom of the tower so that the

bottom, shaped as a ring-like channel, is converted to a mixing chest which provides a strong horizontal circulation. The chlorinated stock is passed without further agitation upward through the tower or chlorinator which is of sufficient size to allow the necessary time for reaction, after which the stock is discharged directly to a vacuum filter. In the succeeding stages involving alkali extraction and hypochlorite bleaching, the chemical is mixed with the pulp from the washer, after which the pulp may be shredded, mixed thoroughly in a double-shaft pulp mixer, and then passed into towers of either the up-flow or down-flow type. The retention time in the tower is varied to secure the desired reaction. The continuous process is best adapted to mills where there are few changes in the grade of pulp produced, as, for example, in Scandinavian mills making pulp for export.

In batch bleaching, chlorination is carried out in vertical reaction cells equipped with a draft tube and an impeller to assist in agitation of the stock (Kamyr batch bleacher), in vertical cells equipped with a draft tube and helicoid screw for moving stock up through the tube (Fletcher type), or in shallow vessels (Bellmers) equipped with a screw propellor for moving the stock between partitions in the bleacher. The chlorine is added directly at the impeller, or first mixed with water in an injector and then the mixture added at the impeller. The caustic extraction is generally carried out at high density, generally in a Fletcher-type cell equipped with draft tube and helicoid screw. The final treatment with hypochlorite may be done in a special beater or high-density bleaching cell. Batch handling is well adapted for the alkaline extraction and final hypochlorite stages, and is well suited for mills making a number of different grades of bleached pulp. In the latter case, it is desirable to have the bleach plant set up on a flexible basis so that any of the stages can be by-passed.

All equipment used in the chlorination stage must be acid-resistant; that is, it must be constituted of stainless steel, rubber-lined iron, or tile-lined concrete. Wood may be used in some places. In the caustic extraction stage, the equipment may be of steel or cast iron construction. Tile-lined towers are frequently used for the hypochlorite stages.

Number of Stages in Multistage Bleaching

In general, the more stages used in bleaching, the lower the bleach consumption, but the greater the cost of handling. The simplest form of multistage bleaching is a two-stage process wherein part of the chlorine is applied by direct chlorination, followed by a water-washing stage, and then by a final stage using hypochlorite bleach. With some pulps, particularly sulfate pulps, an alkali extraction stage with sodium hydroxide is used between the chlorine and hypochlorite stages to remove the alkali-soluble chlorinated lignin residues. In some cases, the whole process may be pre-

ceded by a very light hypochlorite treatment. In other cases a light hypochlorite treatment may be used after chlorination but before the alkali extraction and final hypochlorite. This alters the structure of the chlorinated compounds so that they are more readily soluble in the subsequent alkali extraction.

Sulfite and soda pulps can sometimes be bleached in three stages. On the other hand, four or more stages may be required for sulfate pulps. A large number of stages are required with hard-bleaching pulps in order to reduce the severity of the bleach in any one stage, and thus minimize attack on the cellulose. A general outline of the various combinations which might be used for different commercial pulps is given below. These represent minimum rather than maximum treatment. In some places up to ten stages are used.

Number of stages	Type of stage	Pulp
3	Chlorination, alkali extraction, and hypochlorite	Sulfites and low brightness sulfate pulps
4	Chlorination, alkali extraction, hypochlorite, and hypochlorite	Better grades of sulfite, some sulfate pulps
4	Chlorination, alkali extraction, hypochlorite, alkali extraction, and hypochlorite	Better grades of sulfate

In referring to the number of stages, the alkali-extraction stages are generally included, but the water-washing stages are not.

Sequence is important in multistage bleaching. Generally speaking, the pulp is first chlorinated with about 40 to 70% of the total chlorine, then washed with water, extracted with alkali, washed with water, bleached with the remaining chlorine as hypochlorite, and finally washed again. Alkali may be added at the end of the chlorination stage to neutralize the acidity and convert the excess available chlorine into hypochlorite, but this method is not generally recommended, since it is better to remove the chlorinated reaction products by washing before adding the hypochlorite. In some cases, an alkali extraction may be used between two hypochlorite stages, but this is generally not an economical procedure. The various stages in multistage bleaching are described in the following sections.

Chlorination Stage in Multistage Bleaching

Direct chlorination is generally used in at least one stage of all multistage bleaching processes. Usually between 40 to 70% of the total bleach is added as direct chlorine. This is mixed with the pulp at a consistency of about 3 to 4% at a pH of 1.0 to 2.0.

In the case of sulfate pulps, chlorination is sometimes done in two stages: the pulp is first chlorinated, neutralized, chlorinated again, neu-

tralized, and then washed. Chlorination in two stages is more efficient than the application of a like amount of chlorine in a single stage if an alkaline washing stage is used between the two chlorinations.¹⁰³ A high ratio of the total chlorine can be used in the first chlorination stage without fiber degradation because of the relatively large amounts of chlorine-reactive in crustants which are present at this stage. However, there is more danger of cellulose degradation in a second chlorination stage than in the first chlorination stage. For example, Wells and Schelhorn¹⁰⁴ found that chlorination of sulfate pulp (jack pine) with 5% chlorine in the first stage is far less degrading to the cellulose than chlorination with 1% chlorine in the second stage.

It is desirable to add as much chlorine as possible in the chlorination stage and a minimum of chlorine in the hypochlorite stage, since this preserves the strength of the fiber. The relationship between the amount of chlorine added in the chlorination stage and the per cent bleachable materials removed, brightness attained, and total chlorine consumed has already been shown in Figure V-6 for a sulfite and a sulfate pulp. As can be seen from this figure, there is an optimum amount of chlorine to be added in the chlorination stage, depending upon the type of pulp. Beyond a certain point, the total chlorine consumption increases markedly for an increase in chlorine added in the chlorination stage. Enough chlorine must be added as hypochlorite to decolorize dirt and resin specks, since these are not as susceptible to direct chlorine as they are to hypochlorite. Rue¹⁰⁵ points out that the low concentration of bleach sometimes used in the hypochlorite stage is not sufficient to decolorize these specks. Because of the greater amount of shives, fiber bundles, and bark, in raw, undercooked pulps, it is customary with these pulps to use less chlorine in the chlorination stage and more in the hypochlorite stage, compared to the bleaching of well-cooked pulps. When bleaching pulps to low brightness values, the greatest chlorine economy can be obtained by using a low proportion of chlorine in the chlorination stage and a relatively high proportion of chlorine in the hypochlorite stage.¹⁰⁶

The important factors involved in the chlorination of wood pulps have already been discussed in a preceding section.

¹⁰³ O. S. Sprout and T. W. Toovey, *Paper Trade J.* 124, No. 11: 107-116 (Mar. 13, 1947)

¹⁰⁴ S. D. Wells and F. B. Schelhorn, *Paper Trade J.* 115, No. 7: 69-72 (Aug. 13, 1942)

¹⁰⁵ J. D. Rue, *Paper Trade J.* 104, No. 7: 82-85 (Feb. 18, 1937)

¹⁰⁶ J. D. Rue and S. C. Nagel, *Paper Trade J.* 114, No. 24: 280-287 (June 11, 1942)

Washing with Water and Alkali in Multistage Bleaching

Bleaching is designed to bring the impurities in the pulp to a soluble state where they can be easily removed by washing. Consequently, washing is a very important part of all bleaching operations.

Washing at the end of the bleaching process is necessary to remove solubilized materials, as well as bleach residues, from the pulp. Excess hypochlorite left in the pulp is harmful to dyestuffs and lowers the strength of the pulp. Calcium salts should be removed, since they cause difficulties with sizing of the pulp. Ferric iron left in the pulp leads to discoloration. Alkali left in the pulp will cause "brown" stains on air drying and cause trouble with sizing and coloring.

In multistage bleaching, washing is necessary not only at the conclusion of the bleaching operations but also as an intermediate step between the various stages. The purpose of the washing in this case is to remove the solubilized lignin residues so that they will not consume unnecessary bleach in the subsequent stage. Chlorination would be impractical, were it not for the subsequent washing of the pulp, since chlorine does not decolorize the pulp, but instead renders the impurities soluble in the wash water.

In multistage bleaching, the first stage after chlorination is to dilute the stock to a consistency of about 1%, and then wash the chlorinated pulp with water. At one time, it was necessary to neutralize the chlorinated pulp before washing with water, but this is no longer necessary since the introduction of acid-resistant washing equipment. Washing is often done on two vacuum washers operated in series. These washers may be equipped with pneumatic loaded press rolls which assist in the removal of water.

After the water wash, the pulp is extracted with alkali to remove the remaining chlorinated lignins, natural dyestuffs, and water-insoluble organic acids. By removing these substances with alkali, less hypochlorite is required in the subsequent hypochlorite stage, and a pulp of better color results. Washing with alkali is a necessity in the production of softwood sulfate pulps of brightness values 75 or above. Alkaline extraction is desirable, although not necessary, in the case of sulfite pulps from the standpoint of reduced chlorine consumption and improved pulp quality. Hardwood sulfate pulps apparently do not require an alkaline extraction, even for brightness values well in excess of 80.¹⁰⁷

Large quantities of water are required to wash thoroughly bleached chemical pulps. Thorough washing may require as much as 10,000 gal. for washing, or about 60,000 to 70,000 gal. per ton of pulp in a six- to seven-stage bleaching process for sulfate pulp. However, because of the limitations on water use, frequently no more than 20,000 to 40,000 gal. of water

¹⁰⁷ J. D. Rue and S. C. Nagel, *Paper Trade J.* 115, No. 6: 61-66 (Aug. 6, 1942)

are used in the multistage bleaching of sulfate pulp. Countercurrent washing from stage to stage is commonly used, with the wash waters being re-used as much as possible. Normally, the only flow to the sewer is from the chlorinated pulp washer and the first caustic extraction, since the effluents from these two stages normally contain about 60 to 70% of the impurities. An example of a fairly typical flow chart for the water used in multistage bleaching is as follows:¹⁰⁸

(1) Water from first chlorination stage is used to acidify the unbleached stock before chlorination.

(2) Water from second chlorination stage is used in first chlorination stage.

(3) Water from first alkali extraction is discarded.

(4) Water from second alkali extraction is used in the first alkali extraction.

(5) Water from hypochlorite stage is used in the alkali extraction stage.

(6) White water from paper machine is used in the final hypochlorite stage.

About 4,000 lb. of steam are required for bleaching sulfate pulps in multistage bleaching.

Sodium hydroxide is the most effective alkali for washing. Sodium carbonate, ammonium hydroxide, and sodium metasilicate have also been used, but they are not so effective as sodium hydroxide. Lime is a poor alkali for washing^{109,110} because it tends to precipitate insoluble residues on the fiber which are difficult to bleach. The amount of sodium hydroxide required on the basis of the pulp to dissolve the chlorinated lignin residues depends upon the grade of pulp. Easy bleaching sulfite pulps can be extracted with 0.1 to 1.0% sodium hydroxide, whereas hard bleaching sulfite and sulfate pulps may require as much as 1.5 to 3.0% sodium hydroxide.^{111,112} Complete extraction of sulfate pulps cannot be attained below a pH of 9 to 10.¹¹³ The concentration of the alkali solution generally varies from 0.01 to 0.1%. The consistency of the stock is usually in the neighborhood of 10 to 12%. High consistency is desirable because this increases the alkali concentration for a constant ratio of alkali to pulp.

Washing is largely a physical process in which time and temperature play an important role. Generally speaking, temperature is more important than time.¹¹⁴ The limiting factor is the rate of diffusion of alkali into the

¹⁰⁸ J. N. Swartz, *Pulp Paper Mag. Canada* 47: 203-220, Convention Issue (1946)

¹⁰⁹ G. C. Arnold, F. A. Simmonds and C. E. Curran, *Paper Trade J.* 107, No. 10: 32-36 (Sept. 8, 1938)

¹¹⁰ M. W. Phelps and J. Schuber, *Paper Trade J.* 106, No. 8: 81-84 (Feb. 24, 1938)

¹¹¹ M. W. Phelps and J. Schuber, *Paper Trade J.* 106, No. 8: 81-84 (Feb. 24, 1938)

¹¹² F. Loeschbrandt, *Finnish Paper Timber J.* 668-671 (Sept. 15, 1938)

¹¹³ F. Loeschbrandt, *Bleaching of Sulfate Pulp*, translated by E. Martin, reprinted by TAPPI (1941)

¹¹⁴ F. Loeschbrandt, *Bleaching of Sulfate Pulp*, translated by E. Martin, reprinted by TAPPI (1941)

fiber and the diffusion of dissolved impurities out of the fiber. Ordinarily, extraction is carried out at 25 to 70° C., the higher temperatures being much more efficient. Temperatures above 70 to 80° C. tend to remove increasing amounts of hemicellulosic material, if a high concentration of alkali is used. High temperatures are very desirable if low alkali concentrations are used in order to favor diffusion of alkali to the inner surfaces of the fiber.

Because of the time required in the diffusion of impurities from within the fiber and the tenacity with which the fibers bind impurities in the presence of alkali, double washings with water with a soaking period between are often desirable. Soaking periods are especially recommended after the caustic extraction and after the last hypochlorite treatment.¹¹⁵ These soakings are usually carried out at a consistency of 3 to 3.5% for a period of forty-five to sixty minutes. Once the impurities have diffused through the fiber into the surrounding water, they can be easily removed by simple displacement with clean water.

The chief materials removed by alkali extraction are chlorinated lignins of high molecular weight. The effluent from the caustic extraction is very dark, almost black, in color. At the normal temperatures and concentrations of alkali used, there is very little effect on the hemicellulosic constituents of the pulp, but if the temperature or concentration of alkali get much higher than normal, some hemicellulosic material is removed, and the percentage of alpha cellulose in the pulp is increased. This lowers the yield and results in a soft pulp of high bulking properties. Such treatment is not necessary or desirable in papermaking pulps, but is desired in the case of purified pulps for chemical cellulose. When making these latter grades of pulp, a special alkaline purification is carried out under conditions of temperature and alkali concentration sufficient to remove substantial quantities of beta and gamma celluloscs, as well as other extractives. This subject is discussed later in this chapter under alkaline purification of pulp.

Hypochlorite Stage in Multistage Bleaching

The function of hypochlorite in multistage bleaching is to remove by oxidation the colored residues remaining in the pulp after chlorination and alkali extraction. Chlorinated and extracted pulp still has a dark color because it contains appreciable quantities of residual chlorinated lignin and other colored substances. These substances are readily oxidized by hypochlorite, and consequently the final stage in multistage bleaching is usually a hypochlorite bleach. The degree of previous chlorination and caustic extraction govern the amount of hypochlorite required in the final stage.

¹¹⁵ W. A. Chilson, *Paper Trade J.* 109, No. 25: 331-333 (Dec. 21, 1939)

The factors involved in the hypochlorite stage of multistage bleaching are very similar to those in straight hypochlorite bleaching. There is one difference in that the extracted pulp entering the hypochlorite stage is more susceptible to attack than the original pulp because of the small amount of impurities in the fiber and the higher degree of reactivity of the cellulose. Because of this susceptibility to attack, it is desirable to bleach at a pH of 9 or above and at relatively low temperatures. The amount of bleach used in the final stage should not be more than about 0.7 to 0.8% active chlorine on the weight of the pulp.

In the case of sulfate pulp, the hypochlorite treatment may be split into two stages. The first stage is generally carried out with relatively strong hypochlorite and high densities for a short period. The final stage is carried out with a small amount of chlorine at low density for a relatively long period.

If no alkali extraction is used after the chlorination stage, hypochlorite bleaching in the final stage should be carried out at a relatively high alkali concentration in order to increase the solubility of the chlorinated lignins.¹¹⁶ It is more desirable, however, to remove these chlorinated lignins by alkali extraction before adding the hypochlorite. An additional alkali extraction between hypochlorite stages may be used if desired. This reduces the chlorine consumption, but, as previously mentioned, has the disadvantage of increasing the over-all cost of bleaching.

Final Treatment of Pulp in Multistage Bleaching

It is accepted practice in some mills, particularly when bleaching sulfate pulps, to give the pulp a final washing with acid by soaking at a pH of 6.0 to 6.5. This facilitates washing, lowers the ash content of the pulp, reduces the alkalinity of the pulp, reduces the foaming tendency of the pulp, and prevents yellowing of the pulp.

In some mills, it is common practice to remove any excess active chlorine from the pulp by the use of reducing substances or so-called anti-chlors, followed by washing to remove the reaction products. This method of treatment was used in the old single-stage hypochlorite bleaching, but has found little use in modern multistage bleaching processes, since it is considered a waste of bleaching agent. Among the substances which have been used are sulfites, bisulfites, sulfides, polysulfides, sulfurous acid, and thio-sulfates. Usually the anti-chlor is added in excess to the stock toward the end of the bleaching period and allowed to react until no blue coloration is obtained with potassium iodide-starch indicator. This removes the last traces of hypochlorous acid, hypochlorite ion, and free chlorine from the stock.

¹¹⁶ F. Casciani, *Paper Ind.* 25, No. 4: 427-430 (July, 1943)

Sulfurous acid¹¹⁷⁻¹¹⁹ and clear filtered sulfite cooking acid have been suggested as pulp washing agents. These act as anti-chlors, as mentioned above, protecting the fibers from the harmful effects of residual chlorine. They also reduce ferric iron to ferrous iron, which is more readily separated at the pH existing in the acid washing. Where sulfur dioxide washing is practical, between 0.75 to 1.0 lb. of sulfur dioxide is used for each 100 lb. of pulp, and the pulp is allowed to soak for about 20 to 30 minutes at 3% consistency. Too much acid should be avoided, and the acid should be removed by washing as completely as possible to prevent attack on the screens and paper machine wire.

A final treatment with faintly acid bleach liquor at temperatures higher than normal may be used in the final stage to improve the color and inhibit color reversion.^{120,121} Sodium chlorite, peracetic acid, and peroxide have been used in the final stage to remove the last traces of impurities.

Multistage Bleaching of Alkaline Cooked Pulps with Chlorine Compounds

Bleaching soda pulp is relatively easy. One reason for this is that most soda pulp is produced from hardwoods, and hardwoods (even when cooked by the sulfate process) are generally much easier to bleach than softwoods.¹²² Another factor is that strength is not of paramount importance in soda pulps, which means that the cook can be carried out without regard to strength and the pulp bleached with a fairly drastic hypochlorite treatment.

Soda pulps are sometimes bleached by means of multistage bleaching. Two stages are generally used involving a mild chlorination, followed by a fairly drastic hypochlorite stage. The problems involved are similar to those of sulfate pulps, although far less difficult. It is customary to bleach soda pulp to a brightness of 78 to 80, and there is generally a reduction in brightness of 2 to 3 points on standing. A soft, velvety, bulky, low-strength pulp is produced.

Sulfate pulps can be bleached satisfactorily with single-stage hypochlorite to low brightness values, e.g., low manila shades. No appreciable loss in strength occurs in single-stage bleaching of sulfate pulp up to a brightness of about 50, but generally the pulp begins to lose strength rapidly after a brightness of 55.¹²³ More drastic cooking of the wood improves the bleach-

¹¹⁷ J. C. Baker, U. S. 1,468,693 (Sept. 25, 1923)

¹¹⁸ J. A. Schuber, U. S. 1,820,502 (Aug. 25, 1931)

¹¹⁹ C. A. Blodgett and H. H. Hanson, U. S. 1,822,125 (Sept. 8, 1931)

¹²⁰ German 281,581 (1910)

¹²¹ E. Ebie and G. A. Richter, U. S. 1,470,556 (Oct. 9, 1923)

¹²² J. D. Rue and S. C. Nagel, *Paper Trade J.* 115, No. 6: 61-66 (Aug. 6, 1942)

¹²³ J. D. Rue and S. C. Nagel, *Paper Trade J.* 114, No. 24: 280-287 (June 11, 1942)

ing properties of the pulp by lowering the bleach demand. If cooked to a lignin content of 4% or lower, the bleach demand is approximately the same as that of sulfite pulp.^{124, 125} However, such overcooking is not practical since it lowers the strength of the pulp.

Various reasons have been given for the difficulty in bleaching sulfate pulp with hypochlorite. Among these are: (1) the presence of sulfur in the lignin molecule,¹²⁶ (2) the polymerization of lignin, sugars, and hemicelluloses under the alkaline cooking conditions, (3) the retention of iron or iron compounds, and (4) the presence of coloring matter, small in amount but high in color intensity.¹²⁷ Still another explanation is that a high percentage of the encrustants in sulfate pulp must be removed from the secondary wall, unlike sulfite pulps where there is a more uniform distribution of encrustants.^{128, 129}

Multistage bleaching has been the answer to the bleaching of sulfate pulps and has made possible the production of pulps having a color equal or greater than that of bleached sulfite pulp while retaining the high strength typical of sulfate pulps. Chlorination is the important part of multistage bleaching of sulfate pulps, since chlorine acts selectively on thioglignins, solubilizing the lignin without seriously impairing the strength of the fiber. Alkali extraction is an essential step for removing the chlorinated lignins. Hypochlorite treatment is generally used for solubilizing the remaining chlorinated lignins and for decolorizing certain of the coloring agents not removed by chlorine.

Special cooking conditions are used for making bleachable grades of sulfate pulp. The wood is cooked under more drastic conditions than ordinarily used for making kraft pulps. The pulp should be free of shives and be well washed, since black liquor contains a high proportion of lignin and coloring matter which impair the bleaching of the pulp. The chlorine demand of bleachable sulfate pulps for a multistage bleaching process is generally from 8 to 10% available chlorine.

The number of stages used in the bleaching of sulfate pulp depends upon the original pulp. Easy-bleaching sulfate pulps can usually be bleached in a three-stage process, whereas hard-bleaching sulfate pulps require four, five, six, or more stages involving one or two chlorinations, one or two caustic extractions, hypochlorite, another caustic extraction, hy-

¹²⁴ T. W. Toovey, *Paper Trade J.* 108, No. 25: 317-319 (June 22, 1939)

¹²⁵ W. W. Pigman and W. R. Csellak, *Tech. Assoc. Papers* 31: 393-399 (June, 1948)

¹²⁶ H. Schwartz, J. L. McCarthy and H. Hibbert, *Paper Trade J.* 111, No. 18: 230-234 (Oct. 31, 1940)

¹²⁷ W. F. Holzer, *Paper Trade J.* 99, No. 12: 91-103 (Sept. 20, 1934)

¹²⁸ T. W. Toovey, *Paper Trade J.* 108, No. 25: 317-319 (June 22, 1939)

¹²⁹ Staff of Institute of Paper Chemistry, *Paper Trade J.* 105, No. 27: 375-376 (Dec. 30, 1937)

pochlorite, and sulfurous acid wash. Sulfate pulps in the range of brightness of 65 to 70 can be obtained most effectively with a three-stage bleaching process involving chlorination, caustic extraction, and hypochlorite. By using two hypochlorite stages and inserting a hot caustic extraction between the two stages, the brightness can be increased to about 85. To produce pulps having a brightness over 85, it is necessary (1) to use a double chlorination-alkali extraction, (2) to use a large number of oxidation stages, or (3) to use an oxidizing agent other than hypochlorite, such as chlorine dioxide or sodium chlorite in the final stage.¹³⁰ A typical layout of a sulfate bleachery is shown in Figure V-8.

In multistage bleaching of sulfate pulps, it is customary to chlorinate heavily in the first stage to satisfy the chlorine demand so that no more than 2% chlorine is required as hypochlorite in the subsequent hypochlorite stage. Originally, about 70% of the total chlorine demand was used in the chlorination stage, but this has been reduced to 50 to 60%. Clean, well-cooked pulps can be bleached with 70% of the chlorine demand in the chlorination stage, but only 50% of the chlorine demand should be used in this stage if the pulp is undercooked and "woody."¹³¹ The temperature of chlorination is usually maintained at 25 to 30° C., hot white water being used to maintain the temperature at the proper level. The consistency of the stock at the time of chlorination is generally 3 to 5%, 3.5 being an average figure. High consistencies are desired in the chlorination stage to maintain a low pH (1.5–2.0) and to keep the effective chlorine concentration high, which is important in the case of "woody" stocks. High consistencies cannot be used, however, if agitation is not sufficient to provide good mixing. Retention time in the chlorinator varies from thirty to one hundred twenty minutes, or about one to one and one-half hours as an average.

After chlorination, the stock is washed with water and thickened to a consistency of 15 to 20%. In the Kamyr system, used in some Scandinavian mills, the stock from the chlorination stage is thickened and washed on special filters by displacement, first with hot water and then with hot alkaline liquor.¹³² Water washing before adding alkali results in a reduction in alkali consumption up to 60 to 80%.¹³³ However, under normal conditions of chlorination, only about 40% of the chlorinated lignins are soluble in water,¹³⁴ and hence, alkali extraction is desirable following the water washing. Sodium hydroxide is generally added to the pulp at high consistency in an alkali extraction chest or tower and the pulp extracted under conditions of temperature and alkali concentration which remove the chlo-

¹³⁰ L. E. Russell, *Paper Trade J.* 128, No. 12: 105–108 (Mar. 24, 1949)

¹³¹ J. N. Swartz, *Pulp Paper Mag. Canada* 47: 203–220, Convention Issue (1946)

¹³² J. Richter, *Pulp Paper Mag. Canada* 47, No. 2: 43–58 (Feb., 1946)

¹³³ J. Richter, *Pulp Paper Mag. Canada* 47, No. 2: 43–58 (Feb., 1946)

¹³⁴ R. S. Baker and J. H. Noble, *Paper Mill* 47, No. 62: 20–21 (Nov. 25, 1939)

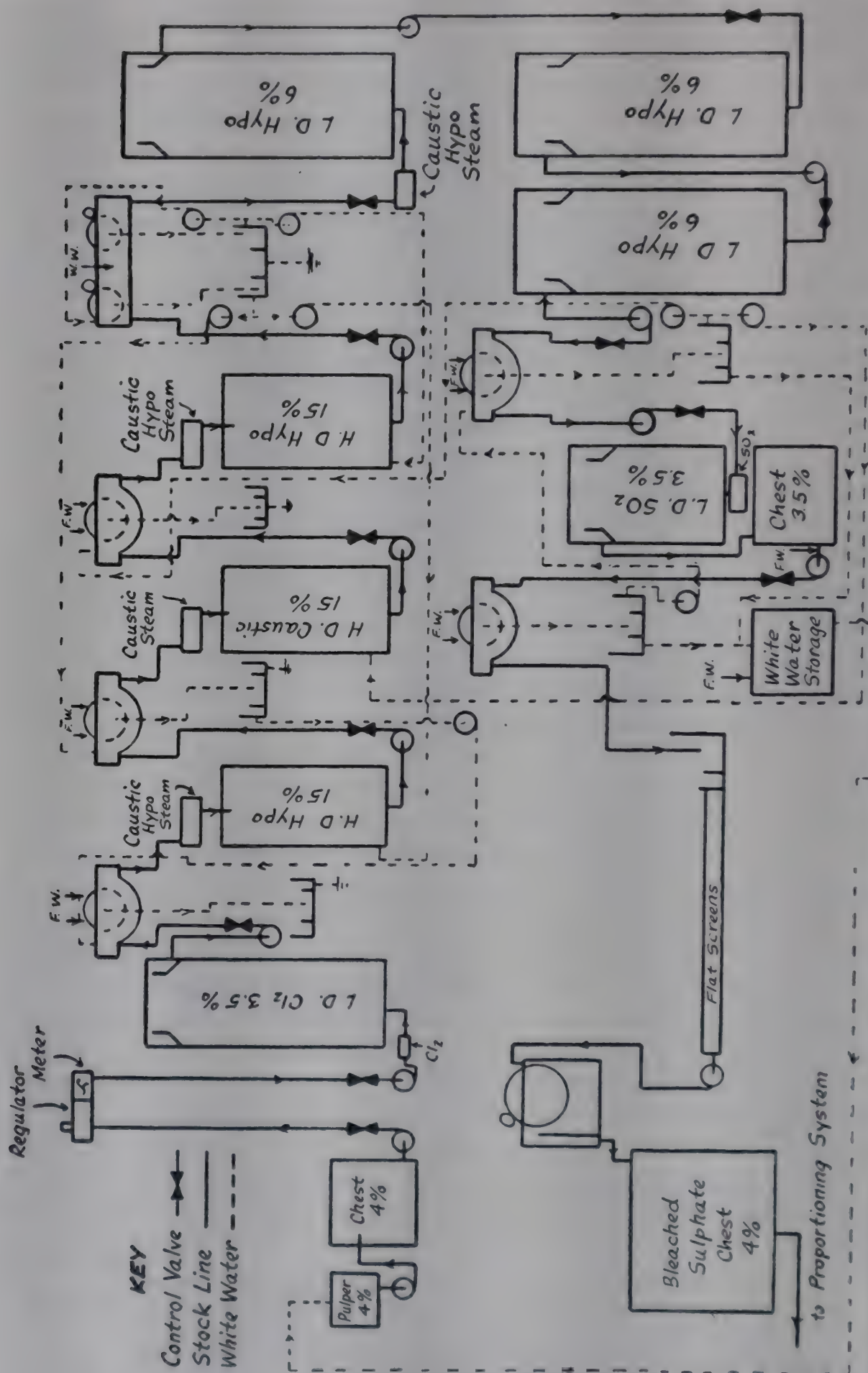


Fig. V-8 Layout of sulphate bleach

minated lignin residues, but do not remove the hemicelluloses to any extent.¹³⁵ High consistency is desirable in this stage to save alkali and also because high consistencies aid in the disintegration and penetration of shives. Normally, between 1.0 to 3.0% sodium hydroxide (pH 10.5–11) is used, based on the weight of the pulp. The extraction is carried out at 60 to 70° C. for a period of thirty to sixty minutes. High temperature (minimum of about 70° C.) is desirable at this point to maintain high efficiency and keep the total chlorine demand within reasonable limits. At the end of the alkali extraction, a water soak is desirable at a consistency of about 3.5% while the stock is under agitation. The pulp is washed and then, in certain cases, given a second chlorination and second alkali extraction, using about one-third as much alkali and a temperature about 10° C. lower than that used in the first extraction.

The next stage in multistage bleaching consists of a single or double treatment with hypochlorite. If two-stage hypochlorite is used, the first stage is generally carried out at a consistency of 10 to 15%, a temperature of 32 to 40° C., and a retention time of one to one and a half hours, using 1 to 2% available chlorine on the weight of the pulp. The pH should be maintained well on the alkaline side during this period. The final hypochlorite stage is generally carried out at a consistency of 6% or less, a 32 to 38° C. temperature, and retention time of three-quarters to 2 to 3 hours, using no more than 0.5% chlorine on the weight of the air-dry pulp. The final hypochlorite bleach is carried to about 85 to 95% exhaustion. A temperature of 25° C. in the final stage was found by McCarthy and Hibbert¹³⁶ to be less degrading to the cellulose than a temperature of 35° C.

After the final hypochlorite stage, the pulp is thickened, washed, and diluted to 3 to 5% consistency and soaked in a dilute sulfurous acid solution at a pH of about 5.5 for one hour. Acid treatment may not be necessary if the pulp is to be used in slush form. However, thorough washing is necessary in all cases to prevent color reversion of sulfate pulps.

The chlorine consumption in the various stages of multistage bleaching of sulfate pulps on the basis of the total amount of chlorine used is generally as follows:¹³⁷ 75% in first chlorination, 10% in second chlorination, 10% in first hypochlorite, and 5% in second hypochlorite. The amount of sodium hydroxide consumed on the basis of the air-dry pulp is as follows:¹³⁸ first caustic extraction, 3%; second caustic stage, 1%; hypochlorite stage, 1%.

¹³⁵ J. D. Rue, *Paper Trade J.* 114, No. 3: 32–34 (Jan. 15, 1942)

¹³⁶ J. L. McCarthy and H. Hibbert, *Tech. Sec. Proc., Canadian Pulp & Paper Assoc.* 35: 237–242 (1949)

¹³⁷ J. V. Savage, *Paper Trade J.* 129, No. 15: 39–40 (Oct. 13, 1949)

¹³⁸ J. V. Savage, *Paper Trade J.* 129, No. 15: 39–40 (Oct. 13, 1949)

Multistage Bleaching of Sulfite Pulps with Chlorine Compounds

Sulfite pulps are the easiest of the chemical wood pulps to bleach. Well-cooked sulfite pulps of low lignin content can be readily bleached to a brightness of 78 to 80 with single-stage hypochlorite without seriously impairing the strength of the fiber.

It was common practice for many years in making white sulfite pulps to produce a "soft" pulp in the cooking operation and then bleach with single-stage hypochlorite. Later, it was found that pulps of better strength and higher yield could be produced at lower cost by cooking a "harder" pulp and then bleaching in a multistage process. Casciani and Storin¹³⁹ point out that two-stage bleaching of a sulfite having a permanganate number of 14.5 to a brightness of 82 results in a saving of 47% chlorine and 80% lime, and produces a pulp of higher strength, less fading, and lower beating rate, compared to single-stage bleaching. Parsons^{139a} has also shown that a saving of 50% chlorine is possible (a reduction from 4.4% available chlorine to 2.2%) by bleaching a sulfite pulp having a permanganate number of 8.5 to a brightness of about 85 in three stages rather than one. The strength and viscosity of the pulp bleached in three stages was higher than that of the pulp bleached in a single stage. The chlorine demand of sulfite pulps in multistage bleaching generally runs from 3 to 8% chlorine.

Easy-bleaching sulfite pulps can be readily bleached in two stages, but three to five stages are best for hard-bleaching grades. Rayon grade sulfite pulps require three or more stages (often two chlorinations and two hypochlorite). It is customary to use enough chlorine in the chlorination stage to reduce the bleachability by about 55 to 65% and then to complete the bleaching with hypochlorite. The results of Kress and Voigtman¹⁴⁰ (see Table X) obtained on a Mitscherlich spruce sulfite (bleach requirement 65%) show a marked decrease in viscosity of the pulp when chlorination is carried beyond about 50% of the bleach demand.

Chlorination of sulfite pulp is more rapid than the chlorination of sulfate pulps. The average retention time in the chlorinators in the case of sulfite pulp is generally thirty to sixty minutes. Chlorination is usually carried out at low consistency (3–4%) and low temperature. The pulp is then washed under acid conditions, after which it may be extracted with dilute sodium hydroxide. Sulfite pulps of papermaking grade do not require extraction with alkali, but treatment with dilute alkali at 85 to 100° F.

¹³⁹ F. Casciani and G. K. Storin, *Paper Trade J.* 115, No. 14: 163–171 (Oct. 1, 1942)

^{139a} J. L. Parsons, *Paper Trade J.* 131, No. 22: 214–222 (Nov. 30, 1950)

¹⁴⁰ O. Kress and E. H. Voigtman, *Paper Trade J.* 97, No. 7: 29–44 (Aug. 17, 1933)

TABLE X

EFFECT OF AMOUNT OF CHLORINE IN CHLORINATION ON THE
PROPERTIES OF SPRUCE MITSCHERLICH SULFITE

Chlorine added, %	Per cent of chlorine demand	Bleachability	Cuprammonium viscosity, cp.	Lignin content, %	Pentosan content, %
0.00	0.0	5.42	94.2	1.42	6.45
0.65	10.0	4.42	91.4	1.22	6.18
1.27	19.6	3.81	94.0	0.92	6.02
2.20	33.8	2.98	91.0	0.49	6.00
3.07	47.2	2.30	94.9	0.21	6.05
3.91	60.1	1.98	72.0	0.14	6.20
4.68	72.0	1.67	63.5	0.08	6.00

is beneficial at this point in neutralizing the acidic materials remaining in the fiber from the chlorination stage, and also by aiding in the removal of a small amount of by-products not removed in the acid wash. Caustic extraction of chlorinated sulfite pulps is desirable when producing pulps of high brightness, in which case it is possible to substitute as much as 1 lb. of caustic for 1 lb. of chlorine.¹⁴¹ The results in Table XI, taken from Parsons and Jackson,¹⁴² show the amount of dissolved material removed from sulfite pulp in a three-stage bleaching process involving chlorination, alkali extraction, and hypochlorite. The values for permanganate consumed by the extract given in the last column show the relative degree to which the extracted organic matter was oxidized. It can be seen that an appreciable amount of material is removed in the alkali extraction stage, and that this material is not greatly oxidized, thus indicating an appreciable saving in chlorine. Average conditions for the commercial extraction of high-brightness sulfite pulps are 12% consistency, 120° F., and a retention time in the tower of about two hours.

After diluting to a consistency of about 3% and washing, the pulp is treated with hypochlorite to satisfy the remaining bleach demand. Treat-

TABLE XI

SOLUBLE MATTER REMOVED IN THREE-STAGE BLEACHING OF SULFITE PULP

Stage	Organic solids removed, g./100 g. pulp	1 N KMnO ₄ consumed/g. organic matter, cc.
Chlorination (2.5% available chlorine)	2.86	84
Wash	0.22	42
Alkali extraction (0.25% NaOH at 25° C.)	0.54	50
Hypochlorite (1.20% available chlorine)	1.10	29

¹⁴¹ J. D. Rue and S. C. Nagel, *Paper Trade J.* 114, No. 24: 280-287 (June 11, 1942)

¹⁴² J. L. Parsons and D. T. Jackson, *Paper Trade J.* 107, No. 14: 165-168 (Oct. 6, 1938)

ment with hypochlorite may be done in two stages. Bleaching in the first stage is generally carried out at high consistency, i.e., about 12%, but at a fairly low temperature, i.e., about 25° C. The final hypochlorite is generally a batch treatment carried out at low consistency, i.e., about 5 to 7%. A retention time as long as four to five hours may be used in the final hypochlorite stage.

After the last hypochlorite treatment, the pulp should be thoroughly washed with clean water, although space requirements sometimes prevent as thorough washing as might be desired. The waste water can be used in any of the preceding washing steps. Acid wash water may be used if desired, although if the pulp has been properly bleached and thoroughly washed, acid souring is not necessary. Omission of the acid souring of the bleached and washed pulp may result in a drop in brightness of about 1 to 2 points, in some cases.¹⁴³

Bleaching Semichemical Pulps with Chlorine Compounds

Ordinarily, semichemical pulps are used unbleached in coarse grades of paper where color is not important. Recently, however, there has been some interest in bleaching semichemical pulps for use in book papers and other grades where lighter color is desirable. Bleaching semichemical pulps presents difficulties arising from the high percentage of lignin (10–18%) and other encrustants which these pulps contain. Ordinarily, the chlorine demand of semichemical hardwood pulp is in the range of 20 to 30%, compared with 3 to 12% for fully cooked pulps.

Single-stage bleaching of semichemical pulps with hypochlorite to brightness levels of 80 plus is not practical. However, moderate brightness pulps in the range of 70 to 75 brightness can be produced from hardwood semichemical pulps using single-stage hypochlorite under approximately the same conditions used for bleaching groundwood¹⁴⁴ (see following section). Yield and strength of the pulp are not greatly affected, yield being 92 to 99% of the unbleached pulp, since only a small amount of the total lignin is removed.

Multistage bleaching with chlorine, alkali extraction, and hypochlorite can be used to produce bleached semichemical pulps having a low lignin content, high strength, and a brightness of 80 or more.^{145–147} Three-stage

¹⁴³ V. Oleskevich, *Pulp Paper Mag. Canada* 48: 123–126, Convention Issue (1947)

¹⁴⁴ F. A. Simmonds and R. M. Kingsbury, *Paper Trade J.* 124, No. 4: 39–47 (Jan. 23, 1947)

¹⁴⁵ F. A. Simmonds and R. M. Kingsbury, *Paper Trade J.* 124, No. 4: 39–47 (Jan. 23, 1947)

¹⁴⁶ J. Traquair and F. G. Rawling, U. S. patent 1,843,467 (Feb. 2, 1932)

¹⁴⁷ F. A. Simmonds and R. M. Kingsbury, *Paper Trade J.* 124, No. 4: 39–47 (Jan. 23, 1947)

bleaching of semichemical pulps from southern hardwoods, e.g., gums and oaks, has been used commercially. In this process, 15 to 18% total chlorine is required, about 90 to 95% of which is added in the chlorination stage.¹⁴⁸ This is followed by an alkali extraction at low temperature (110° F.) and low concentration of alkali so as not to remove the large amount of pentosans which are present in the pulp. In the final hypochlorite stage, about 1% hypochlorite is used. The yield of bleached pulp on the basis of the original wood varies from 57 to 60% for the oaks to 65 to 70% for the gums. The brightness is in the neighborhood of 85 to 88%.¹⁴⁹

Simmonds and coworkers¹⁵⁰ describe the multistage bleaching of semichemical pulps in which the pulp is chlorinated with an amount of chlorine about equal to the lignin content of the pulp. Chlorination of aspen semichemical pulp with this amount of chlorine removes slightly over 50% of the lignin in the pulp (reducing the lignin from about 12% to about 5%) and results in a yield about 88% that of the unbleached pulp. Appreciable loss of carbohydrate material is unavoidable in this process, since considerable water-soluble hemicellulosic material is released. However, about 3.5% additional lignin can be removed with very little further loss of carbohydrate by extraction of the chlorinated pulp with 1% sodium hydroxide. Bleached pulps have faster beating rates and produce stronger papers than the unbleached pulps. They have a rather low freeness and are particularly well suited for making glassine papers. There is an economic advantage in cooking pulp for multistage bleaching to rather low yields, since a reduced yield of unbleached pulp does not materially reduce the yield of bleached pulp.

Bleaching Groundwood with Hypochlorite

Paper mill and affiliated industrial chemists have spent considerable time searching for bleaching agents for groundwood which will produce a satisfactory pulp without too much expense or too great a loss in yield. The problem has been difficult because of the large amount of coloring matter and non-cellulosic materials in groundwood, and because much of the coloring matter is in a form difficult to alter or remove. In certain species, e.g., western hemlock, much of the color is thought to be due to reddish color structures contained in the ray cells¹⁵¹ which are difficult to reach

¹⁴⁸ Round Table Discussion of Bleaching, *Paper Trade J.* 127, No. 24: 21-25 (Dec. 9, 1948)

¹⁴⁹ Round Table Discussion of Bleaching, *Paper Trade J.* 127, No. 24: 21-25 (Dec. 9, 1948)

¹⁵⁰ S. A. Trivedi, R. M. Kingsbury and F. A. Simmonds, *Paper Ind.* 27, No. 10: 1443-1453 (Jan., 1948)

¹⁵¹ C. E. Curran, E. R. Schafer and J. C. Pew, *Paper Trade J.* 101, No. 8: 91-97 (Aug. 22, 1935)

with bleaching agents. Furthermore, some of the constituents of wood which are ordinarily removed in chemical pulping cause trouble in bleaching groundwood pulp; for example, tannins in groundwood may react with iron to form iron tannates which are grayish in color. Treatment with oxalic acid or other acids helps to combat discoloration due to these tannates.

Treatment of softwood groundwood with hypochlorite causes marked yellowing of the pulp with little or no increase in brightness. Hardwood groundwood, e.g., birch, aspen, sugar maple, and yellow poplar, can, however, be bleached to a brightness range of 70 to 75 (an increase of 18 to 24 points) using about 10% available chlorine as hypochlorite. The secret of the process depends upon retarding the rate of reaction in the initial stages when chlorine is normally consumed rapidly by the pulp. This is done by suitable choice of consistency, temperature, and alkalinity.

In bleaching hardwood groundwood with hypochlorite, the temperature should be maintained between 25 to 35° C.¹⁵² The density should not exceed 6%. The amount of alkali used, which is the most important factor of all, should be sufficient to maintain a pH of 11 to 12 at the start of the reaction, and no less than 8 at the end of the reaction. Sodium silicate is beneficial as a buffer. The reaction should be stopped somewhat short of complete chlorine consumption. Acid treatment (sulfur dioxide) may be used at the end of the reaction to increase the brightness.

The yield of bleached hardwood groundwood is in the range of 96 to 100% of the unbleached pulp for 10% available chlorine added as hypochlorite. The bleached pulp is not very stable, tending to lose about 4 to 11 points in brightness on exposure to carbon arc light for about one hour. However, because of the high brightness increase obtained on bleaching and because the color curve has been changed, the pulp still appears relatively bright after exposure. The strength of the pulp is increased slightly on bleaching.

Bleaching Groundwood and Other Pulps with Peroxide

Peroxides, such as hydrogen peroxide and sodium peroxide, or mixtures of the two, have come into prominent commercial use during the past few years. Their use for the bleaching of groundwood has met with appreciable success; and peroxide bleaching techniques are presently being investigated for semichemical pulps, agricultural wastes, and straight chemical pulp.

Properties of Peroxides

Hydrogen peroxide is commercially available in water solution of either 35 or 50% by weight. The 35% solution contains 16.5% active

¹⁵² R. M. Kingsbury, E. S. Lewis and F. A. Simmonds, *Paper Trade J.* 126, No 24: 272-276 (June 10, 1948)

oxygen, and the 50% solution contains 23.5% active oxygen. Sodium peroxide is a pale yellow granular solid containing about 96% sodium peroxide and 20% active oxygen. It is a very active oxidizing agent, but is quite stable so long as it is kept dry. Sodium peroxide has been used more widely than hydrogen peroxide, but there is very little difference in the cost or bleaching effect obtained with the two peroxides. One pound of sodium peroxide is equivalent in active oxygen and alkali content to 1.21 lb. of 35% hydrogen peroxide plus 1.02 lb. of sodium hydroxide.

Steps in Peroxide Bleaching

The bleaching of groundwood with peroxide is done in a single-stage treatment which consists of subjecting freshly ground pulp to peroxide under controlled conditions of temperature, alkalinity, and consistency. The peroxide bleaching process consists of three steps: (1) rapid and thorough mixing of the peroxide bleaching solution with the pulp, (2) storage of the mixture until bleaching has gone to completion, and (3) treatment of the pulp with a reducing and neutralizing agent to destroy the residual trace of peroxide remaining in the pulp. There is no washing of the pulp. Either a semicontinuous or continuous process can be used, depending upon the output of bleached mechanical pulp desired. Equipment used in peroxide bleaching should be made from stainless steel, acid-proof tile, concrete, transite or rubber-lined steel for best results. Wood or silicate coated iron equipment is sometimes used.

Reactions in Peroxide Bleaching

The active agent in peroxide bleaching is believed to be the HO_2^- ion, which is derived from the ionization of hydrogen peroxide as follows:



The reaction between the HO_2^- ion and the pulp constituents is not well understood at present, but it probably involves a selective reaction with the organic coloring matter or lignin in the pulp. Lignin is little affected, although there are indications of a change in the methoxyl content. Jones¹⁵³ deduces that peroxide attacks lignin through the carbonyl groups since methylation of the lignin inhibits the reaction.

Peroxide has little effect on cellulose,¹⁵⁴ and consequently the yields are normally 98 to 102% of the unbleached pulp, part of the yield being derived from the bleaching residues left in the pulp. There is no loss of strength of groundwood on bleaching with peroxide.

¹⁵³ G. W. Jones, *Tappi* 33, No. 3: 149-160 (Mar., 1950)

¹⁵⁴ H. Staudinger and I. Jurisch, *Papier-Fabr.* 35, No. 49: 459-462 (Dec. 3, 1937)

Variables in Peroxide Bleaching

The results obtained from peroxide bleaching depend upon the species of wood, age of wood, and conditions of bleaching. Some hardwoods, particularly poplar, exhibit the best response to peroxide bleaching. However spruce, balsam fir, birch, pine, and other woods can be bleached with success. In so far as the softwoods are concerned, balsam has the best response, spruce next, and pines the poorest response.¹⁵⁵ The highly colored woods native to the west coast and a few eastern woods (hemlock) respond rather poorly. Optimum results are obtained if the pulp is bleached immediately after grinding. A short pretreatment of groundwood with neutral hypochlorite before bleaching has been found¹⁵⁶ to increase the efficiency of the peroxide bleaching.

Peroxide is catalytically decomposed in the presence of iron, copper, lead, and certain enzymes (catalase). In order to inhibit the catalytic effects of traces of these metals and to stabilize the bleach, sodium silicate and magnesium sulfate are added to the peroxide while making up the bleach liquor.¹⁵⁷ This controls the active oxygen release at a rate compatible with that at which it can be taken up by the pulp, thus preventing loss of oxygen to the atmosphere or loss in unnecessary consumption by side reactions. As already mentioned, sodium silicate also has a desirable buffering effect on the bleaching reaction. A typical bleach liquor composition is given in Table XII.¹⁵⁸ Each chemical is added to the mixing tank in the order given

TABLE XII
TYPICAL SODIUM PEROXIDE BLEACH LIQUOR COMPOSITION

Chemical	Amount, % by weight
Epsom salts (commercial)	0.025
Sodium silicate (tech. 42 Bé)	5.0
Sodium peroxide (96%)	2.0
Sulfuric acid (tech. 66 Bé)	1.4

and is completely dissolved before the next chemical is added. The finished bleach liquor usually is stored in tanks from which it is withdrawn as needed. The equivalent active oxygen formula using mixed peroxides would be 0.99% sodium peroxide and 0.857% hydrogen peroxide (50%), no sulfuric acid being needed. The all-hydrogen peroxide formula would

¹⁵⁵ W. E. Stobo and J. K. Russell, *Pulp Paper Mag. Canada* 48, No. 3: 224-232, Convention Issue (1947)
¹⁵⁶ R. L. McEwen, *Paper Trade J.* 122, No. 17: 179-183 (Apr. 25, 1946)
¹⁵⁷ J. S. Reichert, D. J. Campbell and R. T. Mills, *Paper Trade J.* 118, No. 15: 125-128 (Apr. 13, 1944)
¹⁵⁸ D. W. Peat, *Pulp Paper Mag. Canada* 51, No. 3: 218-227, Convention Issue (1950)

include 1.70% of hydrogen peroxide (50%) and 1.01% of caustic soda. The same amount of epsom salts and sodium silicate is used in all formulas.

The bleaching action is characterized by a high rate of exhaustion of peroxide in the initial stages, followed by a lower rate toward the end of the reaction.¹⁵⁹ Brightness appears to be developed in two stages, a very rapid stage, followed by a slower development of brightness. Because the major part of the bleaching action occurs in the early stages, rapid and thorough mixing of the bleach liquor with the pulp is essential. Bleaching is then allowed to continue to about 90% consumption of bleach.

The amount of peroxide used depends upon the results desired, and normally between 1 to 2% of sodium peroxide (or equivalent of hydrogen peroxide) is used. Reichert¹⁶⁰ obtained the following results on bleaching groundwood, using increasing amounts of sodium peroxide at 90° F. and 5% consistency.

Sodium peroxide, %	Points increase in brightness, G.E.
1.0	6-7
1.5	8-9
2.0	10-11

Stobo and Russell¹⁶¹ obtained a brightness of 70 G.E. with a consumption of peroxide equivalent to 0.41% active oxygen (2% sodium peroxide) on the basis of the oven-dry pulp.

Peroxides are relatively stable in acid solution, the rate of decomposition increasing with increasing *pH*. Groundwood pulps are acid (*pH* 4.5 to 5.0) and consequently, adjustment of the pulp with alkali is necessary in order to obtain satisfactory bleaching. The successful use of peroxide for bleaching requires a careful control of the amount of alkali applied to the pulp on a dry basis.¹⁶² This factor is much more important than the starting *pH*, due to the fact that the system is buffered by sodium silicate. If sodium peroxide is used alone, sulfuric acid must be added to neutralize a portion of the caustic soda resulting from the addition of sodium peroxide to water. When hydrogen peroxide is used alone, alkali (caustic soda or sodium silicate) must be added. If sodium peroxide and hydrogen peroxide are used together, approximately equal percentages of each may be used, the desired alkalinity being derived from the sodium peroxide and the hydrogen peroxide being used to fortify to the desired ac-

¹⁵⁹ W. E. Stobo and J. K. Russell, *Pulp Paper Mag. Canada* 48, No. 3: 224-232, Convention Issue (1947)

¹⁶⁰ J. S. Reichert, *Paper Trade J.* 105, No. 15: 143-148 (Apr. 12, 1945)

¹⁶¹ W. E. Stobo and J. K. Russell, *TAPPI Bulletin* No. 76 (Feb. 26, 1947)

¹⁶² C. E. Curran, E. R. Schafer and E. C. Pew, *Paper Trade J.* 101, No. 8: 91-97 (Aug. 22, 1935)

tive oxygen concentration,^{163, 164} no extra alkali being required. Reichert and Pete¹⁶⁶ report that maximum brightness increase and minimum bleaching time are obtained at a starting pH between 10.0 to 10.5, or an alkalinity calculated as 1.2 to 1.9% sodium hydroxide based on the moisture-free pulp. It has been reported that different types of wood require bleach liquor of notably different alkalinities for maximum effect.¹⁶⁷

Temperature has an important effect on the rate of bleaching. Maximum brightness is obtained in a range of 40 to 60° C.¹⁶⁸ Lower temperatures tend to extend the bleaching time, and temperatures which are too high lead to a slight color reversion. In general, the bleaching time increases about twofold for every 10° C. (18° F.) drop in temperature.¹⁶⁹

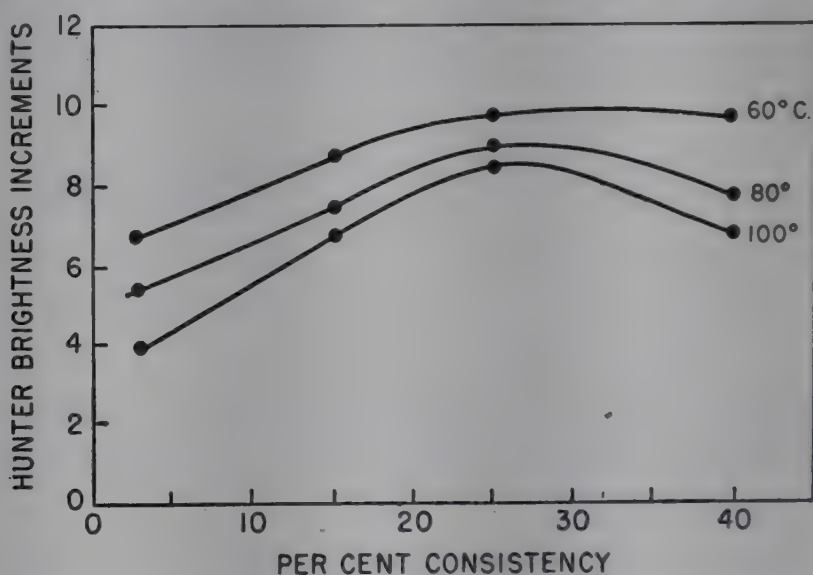


Fig. V-9. Effect of consistency and temperature on brightness increase obtained in peroxide bleaching of groundwood pulp.

The consistency of the pulp during bleaching has a marked effect on the brightness increase obtained for a given amount of chemical, as shown in Figure V-9, for several different temperatures.¹⁶⁸ There is a straight-line relationship between brightness increase and pulp consistency expressed as pounds of water per pound of stock when a constant amount of peroxide is used.¹⁷⁰ High consistency also reduces bleaching time. For example, maximum brightness can be obtained in four hours at 25% consistency, compared to about ten hours at 3% consistency.¹⁷¹ All present commercial

¹⁶³ R. L. McEwen, *Paper Trade J.* 122, No. 17: 179-183 (Apr. 25, 1946)

¹⁶⁴ H. O. Kauffmann, *Paper Trade J.* 121, No. 19: 185-190 (Nov. 8, 1945)

¹⁶⁶ J. S. Reichert and R. H. Pete, *Tappi* 32, No. 3: 97-107 (Mar., 1949)

¹⁶⁷ D. W. Peat, *Pulp Paper Mag. Canada* 51, No. 3: 218-227, Convention Issue 1950)

¹⁶⁸ R. L. McEwen, *Paper Trade J.* 122, No. 17: 179-183 (Apr. 25, 1946)

¹⁶⁹ J. S. Reichert and R. H. Pete, *Tappi* 32, No. 3: 97-107 (Mar., 1949)

¹⁷⁰ J. S. Reichert and R. H. Pete, *Tappi* 32, No. 3: 97-107 (Mar., 1949)

¹⁷¹ R. L. McEwen, *Paper Trade J.* 122, No. 17: 179-183 (Apr. 25, 1946)

trends point toward the adoption of higher and higher consistency operation. Some mills operate at 10 to 12% density, and other mills have operated at 40 to 50%. The majority of the other mills are operated at densities in the neighborhood of 3 to 4%; however, economic considerations favor high-density operation because of increased brightness obtained per chemical dollar, increased speed of passage through the mill, better continuity of operation, and less floor area.

Low-density (3–6%) bleaching is largely a batch operation carried out for a retention time of 3 to 5 hours and a temperature in the range of 30 to 50° C. Moderate density (10 to 15%) and high density (20 to 50%) bleaching are generally of the continuous type, requiring $\frac{3}{4}$ to 5 hours' retention time and a temperature of 40 to 60° C. In high-density systems, the pulp is thickened by deckering, passed through a screw press, blended with the peroxide bleaching liquor in a mixer, and held for a definite retention period in a continuous tower. There is one process, called the steep bleaching process, in which pulp at very high density is impregnated with peroxide bleach solutions of controlled alkalinity and allowed to stand in roll, lap, or crumb form at room temperature for several days until the pulp is ready for use.

At the end of the bleaching period, a reducing and neutralizing agent is added to destroy the trace of peroxide remaining. Acidification of the pulp to a pH of 5.5 to 6.5 increases the brightness of the pulp. Sulfurous acid solution or sulfite cooking acid is ideal for this purpose, since it not only drops the pH but also destroys residual peroxide and reduces ferric iron to the ferrous form. Ordinarily, from 0.3 to 1.0% sulfur dioxide on the dry weight of the pulp is required.

Properties of Peroxide-Bleached Groundwood

Peroxide-bleached groundwood has all the good qualities of regular groundwood, including high opacity, high bulk, resiliency, and good covering properties, and in addition, has a much better brightness. The stability of the bleached pulp to sunlight is not greatly improved, but the stability when stored away from light is very good.^{172, 173} Ordinary groundwood papers lose 2 to 3 points in brightness on drying on the paper machine, but papers made from peroxide-bleached groundwood are more stable. Bleached groundwood has been reported to be about as stable as unbleached sulfite.¹⁷⁴ A color reversion of about 1 per cent is obtained over a 90 day period under ordinary storage conditions.^{174a}

Bleached groundwood forms better on the machine than unbleached

¹⁷² R. L. McEwen, *Paper Trade J.* 122, No. 17: 179–183 (Apr. 25, 1946)

¹⁷³ J. S. Reichert, *Paper Trade J.* 105, No. 15: 143–148 (Apr. 12, 1945)

¹⁷⁴ National Bureau of Standards News Bulletin

^{174a} R. L. Robinson, *Pulp Paper Mag. Canada* 50, No. 10: 80–82 (Sept., 1950)

groundwood, and although the freeness is unchanged or slightly increased, the pulp seems to have a slower drainage rate. The bleached pulp forms sheets which are more homogeneous, finer in texture, less harsh, and smoother than those obtained with unbleached groundwood. These factors make for better printing qualities. The opacity is very nearly the same before and after bleaching,¹⁷⁵ although bleaching to a brightness increase of 5 to 10 points will cause a reduction of about 1 to 2% in printing opacity.¹⁷⁶ Bleached groundwood is well suited for use in such papers as book, magazine, mimeo, tablet, catalog, directory, board liner, and towelling.

Bleaching Other Pulps with Peroxide

To date, bleaching with peroxide has been mainly confined to groundwood pulps, but recent work has indicated that other pulps can be bleached satisfactorily with peroxide.

Peroxide has been suggested as a bleaching agent for semichemical pulps. High yield (72%) aspen neutral sulfite semichemical pulp can be bleached to brightness levels of 74 in a single-stage treatment with 4% sodium peroxide with a loss of only 2 to 4% in yield.¹⁷⁷

Single-stage peroxide bleaching of sulfite pulp has been investigated, and it is indicated that low permanganate number sulfite pulps may be bleached by this method to the brightness range of 70 to 80 G.E., with yields in the neighborhood of 100%.¹⁷⁸ Peroxide bleaching can also be used in the final stage of multistage bleaching of sulfite and sulfate pulps after a preliminary treatment of the pulp with chlorine, hypochlorite, chlorine dioxide, or chlorite. Pulps of brightness 80 to 85 or superbleached pulps of 85 to 90 brightness can be obtained. The peroxide bleaching is best carried out at moderate or high density. Chemical pulps require longer times and higher temperatures than do groundwood pulps, but, in general, the same statements made earlier regarding variables and procedures apply to the peroxide bleaching of chemical pulps. Two very important variables in determining the final brightness are the original pulp brightness and the permanganate number of the pulp. The degree of brightness permanence obtained when peroxide is used in the final stage is better than that obtained when other bleaching agents are used in this stage.

Bleaching with Chlorine Dioxide and Sodium Chlorite

Hypochlorite has enjoyed wide usage as a satisfactory bleaching agent for papermaking pulps for many years. There are, however, several dis-

¹⁷⁵ L. Beeman, F. C. Goodwill and R. Shearer, *Paper Trade J.* 118, No. 24: 33 (June 15, 1944)

¹⁷⁶ R. L. McEwen, *Paper Trade J.* 122, No. 17: 179-183 (Apr. 25, 1946)

¹⁷⁷ R. M. Kingsbury, F. A. Simmonds, R. T. Mills and F. L. Fennell, *Paper Trade J.* 123, No. 11: 124-128 (Sept. 12, 1946)

¹⁷⁸ Private communication from R. L. McEwen

advantages of hypochlorite, the most significant of which is its tendency to attack cellulose and decrease the strength of the fibers. In the range of high brightness, each brightness increment obtained with hypochlorite is obtained at the expense of the strength of the pulp.

Sodium chlorite and chlorine dioxide are selective bleaching agents which are capable of oxidizing the impurities in wood pulps without attacking the cellulose. They can be used to bleach wood pulps to very high brightness levels without appreciable degradation of the cellulose. The reason for this is that chlorite and chlorine dioxide are weaker oxidizing agents than hypochlorite (see Fig. V-1); for example, the oxidation potential of sodium chlorite is about 0.66 at pH 9 and about 0.79 volt at pH 4, compared with 1.2 to 0.95 volt for sodium hypochlorite at the same concentration of available chlorine at pH 7 to 10.¹⁷⁹

Chlorine dioxide and sodium chlorite are expensive bleaching agents and hence are suitable only for the speciality bleaching of rag, flax, and special grades of wood pulps. They are usually used to supplement multistage bleaching with chlorine and hypochlorite in the final stage after the pulp has already been bleached to a brightness level of 65 to 70. By using these bleaching agents in this way, it is possible to develop high-strength and high-viscosity pulps at brightness levels of 85 to 92 and higher. The viscosity and the strength of the pulp tend to remain almost constant over the entire brightness range. These agents are especially well suited for the bleaching of high brightness sulfate pulps which are ordinarily difficult to bleach to high brightness levels without lowering the strength.

Use of Chlorine Dioxide

Chlorine dioxide has found use in the laboratory for isolating the total carbohydrate (holocellulose) fraction of wood. When properly used, there is very little degradation of the cellulose. For example, Staudinger and Jurisch¹⁸⁰ found that purified cotton can be treated in a 0.25% solution of chlorine dioxide for 24 hours with only a slight drop in the degree of polymerization (from 1440 to 1050) compared with a large drop which occurs in chlorine water. In the bleaching of wood pulps under normal conditions, there is practically no change in the viscosity, copper number, and hot alkali solubility of the pulp.¹⁸¹

Within recent years, there has been considerable interest in the use of chlorine dioxide as a commercial bleaching agent, although the widespread use of this material has been retarded by high cost and difficulty in manu-

¹⁷⁹ M. C. Taylor, J. F. White, G. P. Vincent and G. L. Cunningham, *Ind. Eng. Chem.* 32, No. 7: 899-903 (July, 1940)

¹⁸⁰ H. Staudinger and I. Jurisch, *Papier-Fabr.* 35: 462-469 (1937)

¹⁸¹ O. Samuelson and C. Ramsel, *Svensk Papperstidn.* 53, No. 6: 155-163 (Mar. 31, 1950)

facture. Chlorine dioxide is exploded by light, contact with mercury, contact with organic matter, or by electric spark. To reduce the hazards of working with this material, it is necessary to dilute with an inert gas (air or nitrogen) to a concentration of about 4% chlorine dioxide.

The classical laboratory method of generating chlorine dioxide has been by mixing crystalline oxalic acid, sodium chlorate, water, and sulfuric acid, and heating the mixture, whereupon a gaseous mixture of chlorine dioxide and carbonic acid is evolved. This method is, however, too expensive for commercial application. Recently, chlorine dioxide has been made commercially in Sweden and Germany (Holst and I. G. Farbenindustrie process) by passing sulfur dioxide through a solution of sodium chlorate and sulfuric acid at a temperature of 40 to 50° C.¹⁸² to produce relatively pure chlorine dioxide. The reaction is as follows:



Another process (Persson process) involves the reaction of sodium chlorate with chromic sulfate. The resulting chromic acid is treated with sulfur di-

TABLE XIII

COMPARISON OF CHLORINE DIOXIDE AND HYPOCHLORITE ON BRIGHTNESS INCREASE AND VISCOSITY OF NORTHERN SULFATE PULPS
Chlorine applied 1.0%, pH 9.0, temperature 100° F., consistency 5%

Bleaching time, min.	Chlorine dioxide		Hypochlorite	
	Brightness, G.E.	Viscosity, cp.	Brightness, G.E.	Viscosity, cp.
0	70.0	42	70.0	42
10	81.9
20	82.4
30	83.0	40.3	80.4	31.9
60	83.2	40.1	80.8	28.0
90	83.3	39.8	81.2	26.1
120	83.4	..	81.6	23.4

oxide to regenerate the chromic sulfate. Another process involves the reaction of chlorate and an acid in the presence of methanol.

At present, chlorine dioxide is being used in Sweden in the final stage of multistage bleaching to produce sulfate pulps having brightness values as high as 92 to 93. Chlorine dioxide is a weaker oxidizing agent than hypochlorite,¹⁸⁴ and there is very little attack on the cellulose, as shown by the data in Table XIII.¹⁸⁵ It can be seen from this table that chlorine dioxide gave a brightness increase of 13.3 points for a loss in viscosity of 2 cp., com-

¹⁸² G. Holst, translated from Swedish by A. Heilborn, *Paper Trade J.* 128, No. 1: 7-12 (Jan. 6, 1949)

¹⁸⁴ G. Holst, *Svensk Papperstidn.* 48, No. 2: 23-30 (Jan. 31, 1945)

¹⁸⁵ G. P. Vincent, *Paper Trade J.* 124, No. 26: 289-291 (June 26, 1947)

pared with a brightness increase of 11.6 points for a viscosity loss of 19 cp. for the hypochlorite. Another characteristic of chlorine dioxide bleaching is that the major part of the brightness elevation is attained in a very short period (approximately 10 minutes), compared with the slow bleaching rate of hypochlorite.¹⁸⁶ Another advantage of bleaching with chlorine dioxide is that dirt specks are decolorized more easily than in hypochlorite bleaching. This means that the wood need not be so carefully prepared, and the pulping conditions need not be as severe as when making high brightness pulps by conventional chlorine and hypochlorite multistage bleaching. Another advantage is that chlorine dioxide bleached pulps show less tendency to revert in color than hypochlorite bleached pulps, although this is debatable.

Bleaching with chlorine dioxide can be done at a *pH* of 3.5 to 4.5, although bleaching can also be carried out in the alkaline region (*pH* 8.5–9.5) if necessary to prevent corrosion, by adding small, continuous amounts of caustic to the stock. The temperature of bleaching is generally 50 to 80° C., and the time required to complete the bleaching is generally about 15 to 60 minutes. Jahn and Holmberg^{187–189} found that 0.6 to 0.7 gram of chlorine dioxide were required per gram of wood to completely delignify groundwood, and this required about eight days at 20° C. (in pyridene). However, when used in the final bleaching stage in multistage bleaching of sulfate pulp, there is about 0.5 to 0.8% consumption of chlorine dioxide on the weight of the pulp. Lundberg^{189a, 189b} has shown how chlorine dioxide can be used for the bleaching of a sulfate pulp of permanganate number 8.6 using data taken from a patent granted to K. W. Rosen in 1938. The conditions are as follows:

Stage	Chemical	Amt. of chemical/ ton (#/b.d. ton)	Consist- ency, %	Time, hours	Tempera- ture, °C.
1	Chlorine	114	1.2	0.8	7
2	Sodium hydroxide	120	5	5	95
3	Chlorine	20	1.2	..	7
4	Sodium hydroxide	120	5	2	95
5	Chlorine dioxide	12.2	7	4	30
6	Sodium hydroxide	200	5	1	70
7	Chlorine dioxide	6	7	8	30

¹⁸⁶ G. P. Vincent, *Paper Trade J.* 124, No. 26: 289–291 (June 26, 1947)

¹⁸⁷ E. C. Jahn and C. V. Holmberg, *Paper Trade J.* 114, No. 17: 203–208 (Apr. 23, 1942)

¹⁸⁸ C. V. Holmberg and E. C. Jahn, *Paper Trade J.* 111, No. 1: 1–4 (July 4, 1940)

¹⁸⁹ E. C. Jahn and C. V. Holmberg, *Paper Trade J.* 109, No. 13: 164–169 (Sept. 28, 1939)

^{189a} A. H. Lundberg, *Pulp and Paper* 24, No. 6: 78 (May, 1950)

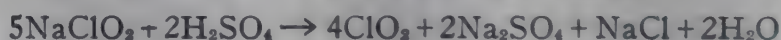
^{189b} A. H. Lundberg, *Pulp and Paper* 24, No. 12: 96 (Nov., 1950)

No substantial amounts of chlorine dioxide have been used directly in the United States for bleaching. However, some chlorine dioxide generated indirectly from sodium chlorite has been used, as shown in the following section.

Use of Sodium Chlorite

Cold alkaline solutions of sodium chlorite have only a mild oxidizing action. In order to obtain satisfactory bleaching, the solution must be acidified to a *pH* of 3 to 5 or activated by the addition of hypochlorite or chlorine. Elevated temperatures are desirable when bleaching with chlorite in order to speed up the bleaching time. Generally, the temperature of bleaching is 40 to 65° C., although temperatures up to 80° C. may be required with sulfate pulps. Generally, from 0.5 to 1.0% chlorine as chlorite is used. The total time of bleaching is ordinarily about two hours.

Acid activation by adjusting the *pH* to about 3.0 to 5.0 with hydrochloric, sulfuric, or acetic acids is sometimes used for batch bleaching. The sodium chlorite is added to the stock first and then acidified. Typical bleaching conditions¹⁹⁰ are as follows: *pH* 4.5 to 5.5, temperature 60 to 80° C., time 2 hours, available chlorine as chlorite 0.5 to 1.0%, consistency 5%. When acidified in the absence of oxidizable material, chlorite produces mainly chlorine dioxide and chlorate in a ratio greater than 2 to 1. In the presence of oxidizable material such as pulp, bleaching is generally accompanied by the formation of chloride.¹⁹¹ The reaction can be expressed by the following simplified equations, depending upon whether HCl or H₂SO₄ is used as the acidifying agent, although the reactions are probably more complicated than indicated by these equations.¹⁹²



Much of the bleaching in acid medium probably results from the reaction of chlorite ion with the oxidizable material in the pulp, although some oxidation is probably accomplished by chlorine dioxide.¹⁹³

If hypochlorite activation is used, from 0.4 to 0.5% sodium chlorite is added to the stock, followed by 0.5 to 1.0% available chlorine added as hypochlorite. The reaction is carried out at a *pH* of 8 to 9.5, a temperature

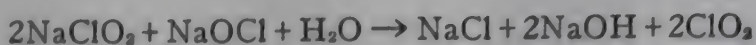
¹⁹⁰ M. C. Taylor, J. F. White and G. P. Vincent, *Tech. Assoc. Papers* 23: 251-262 (June, 1940)

¹⁹¹ M. C. Taylor, J. F. White, G. P. Vincent and G. L. Cunningham, *Ind. Eng. Chem.* 32, No. 7: 899-903 (July, 1940)

¹⁹² M. C. Taylor, J. F. White and G. P. Vincent, *Tech. Assoc. Papers* 23: 251-262 (June, 1940)

¹⁹³ J. F. White, M. C. Taylor and G. P. Vincent, *Ind. Eng. Chem.* 34, No. 7: 782-791 (July, 1942)

of 25 to 40° C., and for a time of two hours.^{194, 195} Slow addition and thorough mixing of the hypochlorite is essential. Intermittent additions of alkali are required to maintain the pH in the desired range. It is believed that chlorine dioxide is evolved under these conditions and that this is responsible for the bleaching action. The main reaction¹⁹⁶ is believed to be as follows:



Conditions are chosen such that the hypochlorite reacts with the chlorite to form chlorine dioxide instead of reacting directly with the cellulose. Hypochlorite activation produces a pulp having good color, but there is more color reversion than in acid activation.

The most satisfactory method of using sodium chlorite for continuous bleaching in large mills is by reaction with gaseous chlorine to produce a solution of chlorine dioxide, which is then used as the bleaching agent. The reaction of the chlorite solution with chlorine may be carried out in a separate reaction tower, or the two may be mixed together just before the point of application. Chlorine dioxide is evolved according to the following reaction:¹⁹⁷



By using a mixture of chlorine dioxide and chlorine gas, operating economies can be affected over the use of pure chlorine dioxide. However, no less than a 1 to 1 ratio of chlorine dioxide to chlorine on an available chlorine basis should be used, and best results are generally obtained with a ratio of 2 to 1 or a ratio of 2.5 to 1.^{198, 199} When used in the proper ratio, the presence of the chlorine enhances the bleaching reaction and there is little or no degrading effect on the cellulose. The desired ratio of mixed gases is obtained by controlling the feed rates of the chlorine and the sodium chlorite solution. The pH of the stock should be maintained at 6 to 8 by the continuous addition of small amounts of sodium hydroxide in order to avoid corrosion.

Stone and Woodside²⁰⁰ bleached sulfite pulp at high consistency in the

¹⁹⁴ M. C. Taylor, J. F. White and G. P. Vincent, *Tech. Assoc. Papers* 23: 251-262 (June, 1940)

¹⁹⁵ G. P. Vincent, *Pulp Paper Mag. Canada* 41, No. 12: 781-782 (Nov., 1940)

¹⁹⁶ K. S. MacLeod, *Pulp Paper Mag. Canada* 51, No. 3: 156-158, Convention Issue (1950)

¹⁹⁷ K. S. MacLeod, *Pulp Paper Mag. Canada* 51, No. 3: 156-158, Convention Issue (1950)

¹⁹⁸ G. P. Vincent, *Paper Trade J.* 124, No. 26: 289-291 (June 26, 1947)

¹⁹⁹ K. S. MacLeod, *Pulp Paper Mag. Canada* 51, No. 3: 156-158 Convention Issue (1950)

²⁰⁰ W. A. Stone and V. Woodside, *Paper Mill News* 47, No. 71: 18-20 (Nov. 20, 1948)

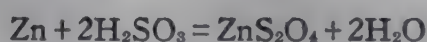
final stage of a commercial multistage bleaching process (after chlorination and caustic extraction), using a mixture of hypochlorite and chlorine dioxide. Practically no decrease in viscosity of the pulp was obtained in bleaching to a brightness of 86 when the ratio of hypochlorite to chlorine dioxide was such that all the hypochlorite was consumed before complete exhaustion of the chlorine dioxide.

Bleaching Groundwood with Reducing Agents

Reducing agents, e.g., sodium bisulfite, sodium hydrosulfite, sulfurous acid, and others, have been used for improving the color of groundwood. These reducing agents can be applied in a crude process involving a spraying, flooding, or roll application of a 2 to 3% solution of reducing agent to pulp on a wet machine so that about 2% of the agent is picked up by the pulp. Whitening of the pulp takes place immediately, but the color reverts slowly on storage and air exposure. The treated pulp has limited application because of the low brightness obtained and the impermanent color.

A newer and better method of bleaching groundwood involves a treatment of the pulp in slush form with zinc hydrosulfite. Zinc hydrosulfite can be readily made in the mill from zinc dust and sulfur dioxide by the following procedure:²⁰¹

- (1) Adding 180 lb. zinc dust to cold water.
- (2) Bubbling SO₂ through the liquid at 60 to 85° F. until the pH reaches 4.0 to 4.2.
- (3) Settling excess zinc and decanting clear liquid.
- (4) Storing clear liquid away from air at temperature of 60° F. until ready for use. Storage under oil will prevent oxidation. The reaction may be expressed as follows:



Zinc hydrosulfite solution can be added directly to the regular stock system by feeding into the stock directly after the grinder. However, no more than 2 lb. per ton can be added in this way without excessive corrosion of equipment.²⁰² A better system involves treatment of the stock in retention chests followed by washing to remove residual corrosive acids from the pulp.²⁰³ The bleaching agent is added to the stock in the retention chamber at 2.25% consistency. Acid-resistant equipment must be used for handling the unwashed stock and effluent from the washers, but once the stock is washed, there is no danger of corrosion on the paper machine.

The amount of zinc hydrosulfite varies from 4 to 10 lb. per ton of newsprint.^{204, 205} The temperature of treatment generally is between 135

²⁰¹ I. H. Andrews, *Pulp Paper Mag. Canada* 46, No. 9: 679-681 (Aug., 1945)

²⁰² R. R. Ferguson, *Paper Trade J.* 127, No. 16: 52-55 (Oct. 14, 1948)

²⁰³ I. H. Andrews, *Pulp Paper Mag. Canada* 46, No. 9: 679-681 (Aug., 1945)

²⁰⁴ I. H. Andrews, *Pulp Paper Mag. Canada* 46, No. 9: 679-681 (Aug., 1945)

²⁰⁵ R. R. Ferguson, *Paper Trade J.* 127, No. 16: 52-55 (Oct. 14, 1948)

to 200° F. Brightness increases up to 200° F., but deterioration of the color takes place if the pulp is held too long at high temperatures. Best results are obtained by buffering the pulp in the pH range of 5.5 to 6.5, using sodium silicate, calcium carbonate, or sodium sulfite.²⁰⁶ Variations in consistency from 1 to 6% have little or no effect on the brightening action. For groundwood papers requiring a high brightness, Andrews²⁰⁷ suggests 3 to 4% zinc hydrosulfite, a temperature of 160 to 165° F., and a retention time of 1.5 to 2.0 hours.

Spruce and fir are most responsive to hydrosulfite, hemlock being bleached with greater difficulty.²⁰⁸ Zinc hydrosulfite is most efficacious in

TABLE XIV

EFFECT OF ZINC HYDROSULFITE ON BRIGHTNESS OF GROUNDWOOD PULPS

Amount of zinc hydrosulfite, %	Treatment		Brightness	
	Temperature, °F.	Time, hours	Western hemlock	Sitka spruce
0	53	59
0.5	80	2.2	57	62.5
	140	0.5	58	63.5
	180	0.3	58.5	64
1.0	80	4.0	58.5	63
	140	1.3	60	64.5
	180	1.0	60.5	65.5
2.0	80	6.5	59.5	63.5
	140	1.8	61.5	65.5
	180	1.5	62	66.5
4.0	80	15.5	60	64
	140	2.5	62.5	67
	180	2.0	63.5	68

the treatment of west coast groundwoods, for example, hemlock and balsam fir, which are lower in brightness and have a more reddish shade than spruce. The process is economical and efficient for a brightness rise of about 6 points,²⁰⁹ that is, an increase in the brightness of western hemlock from 53 to 57 to 59, which is equivalent to the brightness obtained with spruce. The effect of zinc hydrosulfite on the brightness of hemlock and spruce groundwood pulps is shown in Table XIV.²¹⁰ The color improvement persists fairly well on aging in the absence of sunlight, although An-

²⁰⁶ D. W. Peat, *Pulp Paper Mag. Canada* 51, No. 3: 218-227, Convention Issue (1950)

²⁰⁷ I. H. Andrews, *Pulp Paper Mag. Canada* 46, No. 9: 679-681 (Aug., 1945)

²⁰⁸ D. W. Peat, *Pulp Paper Mag. Canada* 51, No. 3: 218-227, Convention Issue (1950)

²⁰⁹ R. R. Ferguson, *Pulp Paper Mag. Canada* 49, No. 8: 85-88 (July, 1948)

²¹⁰ I. H. Andrews, *Pulp Paper Mag. Canada* 46, No. 9: 679-681 (Aug., 1945)

draws²¹¹ found that the brightness of bleached western hemlock reverted from 61 to 54 on aging for three years in the absence of light.

Alkaline Purification of Pulp

Ordinary papermaking grades of pulp contain an appreciable amount of degraded cellulose, pentosans, polyuronides, and hexosans of non-cellulosic nature. These materials are desirable in certain amounts in papermaking pulps, since they increase the yield and improve the sheet-forming qualities of the pulp. There are, however, certain grades of pulp used for special purposes in which these materials are undesirable. These are known as alpha pulps, or alpha cellulose. Purified wood cellulose (alpha pulp) is considered to be a pulp having an alpha cellulose content of 90% or above. The exact alpha cellulose requirement depends upon the end use of the pulp.

Uses for Alpha Pulps

Alpha pulps are used for making vulcanized papers, papers for parchmentizing, papers for resin impregnation, and special papers where permanency is a major requirement. A very important grade is that known as dissolving pulp, which is a highly purified form of cellulose used in the manufacture of rayon, cellophane, methylcellulose, ethylcellulose, nitrocellulose, cellulose acetate, and other cellulose derivatives. Normally, about two-thirds of all the available dissolving wood pulp is used in making rayon, but substantial amounts are also used in making other cellulose derivatives.²¹²

Pulp to be used for rayon manufacture generally has an alpha cellulose content in the range of 88 to 91%. A high percentage of pentosans and other hemicelluloses is objectionable in rayon grade pulp, not because these materials increase the difficulty in xanthation, but because they cause trouble in filtering and also because they are an indication that the morphological structure of the pulp has not been altered sufficiently to obtain the desired reactivity.²¹³ Sulfite pulp containing about 5% pentosans is suitable for rayon manufacture, but ordinary hardwood sulfate pulp containing this amount of pentosans is not satisfactory.²¹⁴ The requirements of a rayon grade pulp are summarized in Table XV.²¹⁵ A low-viscosity pulp is desired in order to reduce the time of aging of the viscose,²¹⁶ but the viscosity must be uniform.

²¹¹ I. H. Andrews, *Pulp Paper Mag. Canada* 46, No. 9: 679-681 (Aug., 1945)

²¹² R. S. Aries, *Paper Trade J.* 130, No. 2: 29-33 (Jan. 12, 1950)

²¹³ E. Heuser, *Tappi* 33, No. 3: 118-124 (Mar., 1950)

²¹⁴ G. Jayme, *Papier-Fabr.* 38: 277 (1940)

²¹⁵ C. W. Tasker and C. E. Libby, *Paper Trade J.* 123, No. 23: 181-190 (Dec. 5, 1946)

²¹⁶ G. A. Richter, U. S. 1,860,432 (May 31, 1932)

TABLE XV

CHEMICAL REQUIREMENTS OF A SUITABLE RAYON GRADE PULP

Alpha cellulose, %	Greater than 88.0
Soluble in alcohol benzene, %	Less than 0.5
Pentosan, %	Less than 5.0
Ash, %	Less than 0.15
Lignin, %	Less than 0.10
Brightness, %	Greater than 85
Viscosity (TAPPI), cp.	1 to 25

The requirements of pulp used in the manufacture of cellulose acetate, nitrocellulose, and similar cellulose derivatives are much more exacting than those for rayon grade pulp. Pulps for these purposes must be relatively free of pentosans, degraded celluloses, and other non-cellulosic materials, because these materials produce a hazy solution, lower the yield, reduce the recovery of chemical, and impair the physical and chemical properties of the cellulose derivative. Ordinary sulfite pulps produce an insoluble residue after acetylation equal to about 10 to 29% of the original pulp, compared with less than 0.1 to 0.2% residue obtained on the acetylation of an especially purified pulp made from cotton linters.^{217, 218} Wood pulps having an alpha cellulose content up to 93 to 96% and a pentosan content as low as 3 to 5% are not suitable for making cellulose acetate because of haze, poor color, and insoluble residues.²¹⁹ Ordinarily, an alpha cellulose content of 94 to 98% and a pentosan content less than about 1.0 to 1.5% are considered necessary in wood pulps for acetylation, the low pentosan content being the more important. Specially purified wood pulps of low pentosan content approach cotton pulps in clarity and lack of insoluble residue when acetyl-

TABLE XVI

COMPARISON OF COTTON PULP AND REFINED SULFITE PULP FOR ACETYLATION

Analysis	Cotton pulp	Highly refined sulfite pulp
Alpha cellulose, %	98.3	93.4
Pentosans, %	1.4
Copper number	0.06	0.69
Ash, %	0.13	0.20
Viscosity (TAPPI), cp.	124	30.6
Resin content, %	0.3
D.P. of nitrate in acetone	1440	1145

²¹⁷ E. Heuser, W. Shockley and J. A. Van den Akker, *Tappi* 32, No. 6: 251-253 (June, 1949)

²¹⁸ G. Jayme and V. Schenck, *Cellulosechemie* 22: 54-56 (1944)

²¹⁹ F. Olsen, *Ind. Eng. Chem.* 30, No. 5: 524-526 (May, 1938)

ated.²²⁰ An analysis of a suitable pulp is given in Table XVI.²²¹ A comparison of two sulfite pulps, one of which is suitable for rayon and the other for cellulose acetate, is given in Table XVII.²²²

Sulfite pulps are considered more satisfactory for making cellulose derivatives than alkaline-cooked pulps, although satisfactory products can be made from alkaline-cooked pulps by a special process, to be described later. Sulfite pulp containing 1% pentosans or less produces a haze-free syrup on acetylation, whereas sulfate pulp of the same pentosan content may produce a very hazy syrup.²²³ The viscosity of the pulp must be carefully controlled, since pulp viscosity determines the viscosity of the cellulose derivative,

TABLE XVII

ANALYSIS OF HARDWOOD SULFITE PULPS SUITABLE
FOR RAYON AND CELLULOSE ACETATE

Analysis	Rayon	Cellulose acetate
Total pentosans	8	2
Resistant pentosans (insoluble in 7% NaOH)	1	0.2
Alpha cellulose	89 to 91	96 to 98

which in turn affects the spraying and brushing qualities and film-forming strength of the derivative.

Effect of Alkali on Pulp Constituents

High alpha pulps are made by extracting pulp (usually a special grade of sulfite) with alkali to remove a large part of the pentosans, degraded celluloses, polyuronides, low molecular weight hexosans, and other objectionable non-cellulosic residues. Alkali acts by peptizing these materials,²²⁴ and also by reacting with the dissolved substances.²²⁵ Acid washing of the pulp after alkali extraction is desirable in reducing the ash content of the pulp. The process of extracting pulp with alkali is often referred to as alkali refining; it is one stage in the multistage process of purification which starts with the pulping of the wood. The final yield of purified pulp varies according to the grade of pulp being made, and may be as low as 29 to 30% on the original wood basis in the case of high alpha pulps for cellulose acetate.

²²⁰ E. Heuser, W. Shockley and J. A. Van den Akker, *Tappi* 32, No. 6: 251-253 (June, 1949)

²²¹ E. Heuser, W. Shockley and J. A. Van den Akker, *Tappi* 32, No. 6: 251-253 (June, 1949)

²²² W. Klauditz, *Holz als Roh- und Werkstoff* 4: 314-325 (1941) through A. Miller, *Paper Trade J.* 124, No. 9: 104-114 (Feb. 27, 1947)

²²³ J. W. McKinney, *Paper Trade J.* 122, No. 4: 36-40 (Jan. 24, 1946)

²²⁴ H. F. Lewis, *Paper Trade J.* 95, No. 21: 239-252 (Nov. 24, 1932)

²²⁵ T. Bergek, S. Gustavsson and E. Lindvall, *Svensk Papperstidn.* 50: 22-28 (June 15, 1947)

Ordinarily, extraction with alkali has relatively little effect on the viscosity of the pulp. Viscosity must, in general, be controlled in the cooking operation. If strong alkali is used, the viscosity may rise, because of the removal of low molecular weight constituents from the pulp.²²⁶ However, strong alkali will reduce the viscosity if allowed to remain in contact with the pulp for long periods of time.

Types of Refining Processes

Results obtained in the alkali refining of any given pulp depend upon the time, temperature, and concentration of alkali used. Extraction may be done in open or closed vessels, at atmospheric pressure, or at higher than atmospheric pressures. There are two general refining methods: (1) the hot process, generally used for the papermaking grades of alpha pulp, in which dilute solutions of alkali (0.5–2.0%) are used at elevated temperature (100–160° C.), and (2) the cold process, generally used for the dissolving grades of alpha pulp, in which strong solutions of alkali (3 to 25%) are used at low temperatures (20–50° C.). The hot refining process generally produces pulps having an alpha cellulose content within the range of 85 to 90%, with an upper limit of about 95 to 96%.²²⁷ The cold refining process will produce pulps having an alpha cellulose content of 98 to 99%. Both processes are discussed in the following sections.

Variables in Hot Alkali Refining

The principal variable in hot alkali refining is the ratio of alkali to pulp. Temperature, time, and concentration of alkali solution are other important variables. Increasing any of these variables tends to increase the alpha cellulose content of the pulp but reduces the yield. It has been shown that the dissolution of pulp in dilute alkali at high temperature is a function of the quantity of alkali consumed during refining, irrespective of the concentration of alkali and the time of refining.²²⁸

Table XVIII²²⁹ shows the effect of varying amounts of alkali (on pulp weight) on unbleached sulfite pulp. Figure V-10 shows the effect of time, temperature, and concentration of alkali solution on the alpha cellulose content of a sulfite pulp which had been prechlorinated to 70% of the chlorine demand.²³⁰ These results show that increasing the amount of alkali increases the alpha cellulose content, but as shown in Figure V-10, the maxi-

²²⁶ G. Goldfinger and H. Mark, *Paper Trade J.* 115, No. 16: 203–205 (Oct. 15, 1942)

²²⁷ G. A. Richter, *Ind. Eng. Chem.* 32, No. 3: 324–328 (Mar. 1940)

²²⁸ T. Bergek, S. Gustavsson and E. Lindvall, *Svensk Papperstidn.* 50: 22–28 (June 15, 1947)

²²⁹ G. A. Richter, *Ind. Eng. Chem.* 33, No. 12: 1518–1528 (Dec., 1941)

²³⁰ L. Rys and A. Bonisch, *Paper Trade J.* 108, No. 19: 225–234 (May 11, 1939)

TABLE XVIII

EFFECT OF AMOUNT OF ALKALI ON UNBLEACHED SOFTWOOD SULFITE
(1.2% LIGNIN) IN HOT REFINING

Temperature 100° C., consistency 6%, time 4 hours

Sodium hydroxide, % on pulp	0	5	10	15
Yield, %	94.3	86.0	83.0
Alpha cellulose, %	88.2	91.9	94.1	94.5
Pentosans, %	4.1	3.5	2.8	2.5
Viscosity (A.C.S.), poises	80	25	18	15
Chlorine requirement as bleach to attain brightness of 90	5.5	4.0	3.5	3.5

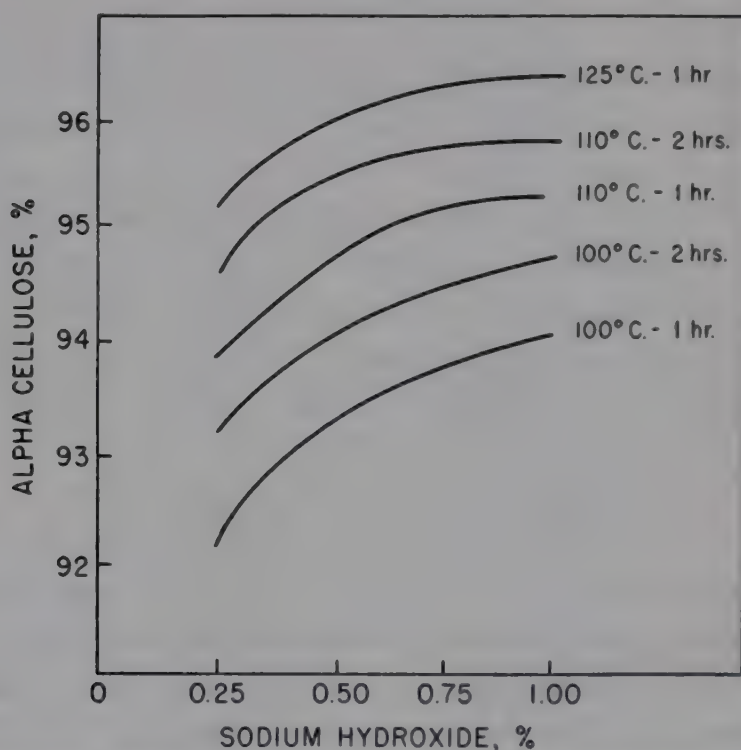


Fig. V-10. Effect of time, temperature, and concentration of alkali on alpha cellulose content of sulfite pulp.

imum upper limit obtainable with hot, dilute alkali is about 96% alpha cellulose. For practical purposes, Coster and Vincent²³¹ list the following conditions as most suitable for producing pulp of a given alpha cellulose content from softwood sulfite pulp (the amount of alkali listed is slightly less than that indicated in Table XVIII):

Extent of purification	Sodium hydroxide on fiber, %	Treatment temperature, °F.
91% alpha cellulose	2	190
93% alpha cellulose	3 to 4	200 to 210
96% alpha cellulose	8 to 10	Greater than 212

²³¹ N. W. Coster and R. Vincent, *Paper Trade J.* 119, No. 11: 117-119 (Sept. 21, 1944)

The loss of yield in hot refining is roughly about 3% for every increase in alpha cellulose content of 1%²³²

Hot refining is suitable for sulfite pulps, but is not effective with ordinary sulfate pulp. When refining sulfite pulp, the hot alkali is generally applied to the partially bleached pulp after chlorination. Then the pulp is bleached with hypochlorite under mild conditions. It has been stated^{233, 234} that fully bleached pulp does not possess sufficient resistance to hot refining because of the increase in solubility resulting from oxidation of the fiber. This, however, appears to depend upon the type of oxidized fiber present; it has been found that carboxyl groups have a higher resistance to hot alkali than carbonyl groups.²³⁵ This agrees with the reported fact that pulps treated with oxidizing agents in alkaline medium are less soluble in alkali than pulps treated with oxidizing agents in acid medium (high copper number).²³⁶

Variables in Cold Alkali Refining

Cold refining differs from hot refining in that stronger solutions of alkali and lower temperatures are used and in that the refining is generally done on the fully bleached pulp. Cold refining is suitable for sulfite and sulfate pulps, hardwoods or softwoods. It is used for the preparation of dissolving grades of alpha pulp. Cold refining is more effective than hot refining in removing non-cellulosic materials; pentosans are more soluble in the cold. Often the final yield is higher than that obtained in hot refining because there is less degradation of the cellulose.

Hot refining appears to remove material only from the easily accessible amorphous regions of the fiber, but the alkali in cold refining appears to penetrate into the crystallites, causing intramicellar swelling.²³⁷ The fiber tends to swell in strong alkali at low temperatures, and this results in handling difficulties.

High consistency is desirable in cold refining in order to reduce the amount of alkali required. However, for a constant alkali concentration, the higher the consistency, the lower the alpha cellulose content, because there is less alkali present based on pulp weight.²³⁸ Alkali recovery is necessary in cold refining to keep the process economical.

²³² N. W. Coster and R. Vincent, *Paper Trade J.* 119, No. 11: 117-119 (Sept. 21, 1944)

²³³ G. Jayme, *Paper Trade J.* 106, No. 21: 297-302 (May 26, 1938)

²³⁴ L. Rys and A. Bonisch, *Paper Trade J.* 108, No. 19: 225-234 (May 11, 1939)

²³⁵ T. Bergek, S. Gustavsson and E. Lindvall, *Svensk Papperstidn.* 50: 22-28 (June 15, 1947)

²³⁶ C. Birtwell, D. A. Clibbens and A. Geake, *J. Textile Inst.* 16: T13-52 (1925)

²³⁷ T. Bergek, S. Gustavsson and E. Lindvall, *Svensk Papperstidn.* 50: 22-28 (June 15, 1947)

²³⁸ L. Rys and A. Bonisch, *Paper Trade J.* 108, No. 19: 225-234 (May 11, 1939)

TABLE XIX

EFFECT OF ALKALI CONCENTRATION IN COLD ALKALI REFINING
OF UNBLEACHED SULFITE PULP

Temperature 25° C., consistency 5%, time 1 hour

	A	B	C	D	E	F	G	H
Concentration of sodium hydroxide, %	0	2.5	5.0	7.5	10	15	25	40
Yield, %	96.5	95.0	92.2	88.8	86.5	88.0	89.8
Alpha cellulose, %	87.7	88.8	91.0	93.7	95.2	96.9	96.3	93.8
Pentosans, %	4.5	3.25	3.07	1.68	0.94	0.93	0.93	2.05
Viscosity (A.C.S.), poises	60	50	48	46	48	41	35	38
Chlorine required as bleach to attain a brightness of 90	5.5	4.5	4.0	4.0	4.0	4.0	4.0	4.0

The concentration of alkali is an important variable in cold alkali refining. As a general rule, increasing the concentration of the alkali solution increases the alpha cellulose content of the pulp up to a concentration of 15 to 20% sodium hydroxide, at which point the alpha cellulose content passes through a maximum and the yield passes through a minimum. Tables XIX²³⁹ and XX²⁴⁰ present data from two different sources showing the effect of alkali concentration on samples of unbleached and prechlorinated sulfite pulps. As noted previously, commercial cold refining is generally done on fully bleached pulp.

With solutions of sodium hydroxide stronger than 5% and temperature levels of about 60° C., the removal of pentosans and hemicelluloses is more complete as the temperature of treatment is reduced.²⁴¹ A 5% solution of sodium hydroxide at 10° C. is more effective in removing pentosans and degraded cellulose than a 7% solution at 30° C.²⁴² A 2.5 N sodium

TABLE XX

EFFECT OF ALKALI CONCENTRATION IN COLD REFINING
OF PRECHLORINATED SULFITE PULP

Temperature 20° C., consistency 5%

NaOH concentration, %	Alpha cellulose content, %
0	88.2
2.5	89.9
5.0	92.0
7.5	95.0
10.0	97.2

²³⁹ G. A. Richter, *Ind. Eng. Chem.* 33, No. 12: 1518-1528 (Dec., 1941)
²⁴⁰ L. Rys and A. Bonisch, *Paper Trade J.* 108, No. 19: 225-234 (May 11, 1939)
²⁴¹ G. A. Richter, *Ind. Eng. Chem.* 33, No. 12: 1518-1528 (Dec., 1941)
²⁴² G. A. Richter, *Ind. Eng. Chem.* 33, No. 12: 1518-1528 (Dec., 1941)

TABLE XXI

EFFECT OF TEMPERATURE IN COLD REFINING OF BLEACHED
SULFITE PULP (88% ALPHA CELLULOSE)

Concentration of alkali solution 7.5%, consistency 5%

Temperature, °C.	Alpha cellulose, %	Yield, %
20	96.94	87.6
30	97.23	86.5
35	97.15	86.5
40	97.00	86.8
45	96.42	87.5
50	95.42	90.0
55	95.64	89.2
60	95.91	88.7
70	96.32	88.3
80	96.74	87.5

hydroxide solution has its maximum solubility for degraded cellulose at $-5^{\circ}\text{C}.$; a 3.0 *N* solution of sodium hydroxide has its maximum solubility at $15^{\circ}\text{C}.$ ^{243, 244} The effect of temperature on the alpha cellulose content and yield of bleached sulfite pulp after refining with strong alkali (7.5% solution) is shown in Table XXI.²⁴⁵ A temperature of $50^{\circ}\text{C}.$ appears to be a critical point at which the lowest alpha cellulose content and highest yield are obtained.

Refining of Sulfite Pulp

Commercial pulps differ widely in the ease with which they can be purified with alkali. The ease of purification depends upon (1) the strength of the linkage between the cellulose and the pentosans and other non-cellulosic carbohydrates, (2) the polydispersity of the fiber constituents, and (3) the morphological and fine structure of the fiber.^{246, 247} These properties of the pulp depend upon the type and severity of the cooking process. Drying of the pulp reduces the solubility of pentosans in alkali, but increases the solubility of the cellulose.²⁴⁸ Bleaching tends to increase the solubility of the pentosans.

Sulfite pulps obtained from the softwood species are the easiest to refine by alkali. This is due to the fact that softwood sulfite pulps contain as little as 2 to 5% pentosans, compared with about 10% pentosans for hardwood sulfite, about 10% pentosans for softwood sulfate, and about

²⁴³ G. F. Davidson, *J. Textile Inst.* 27, No. 7: 144-168 (July, 1936)

²⁴⁴ G. F. Davidson, *J. Textile Inst.* 25, No. 5: T174-196 (May, 1934)

²⁴⁵ L. Rys and A. Bonisch, *Paper Trade J.* 108, No. 19: 225-234 (May 11, 1939)

²⁴⁶ A. Meller, *Paper Trade J.* 121, No. 13: 119-131 (Sept. 27, 1945)

²⁴⁷ E. Lindpainter, *Melliand Textilber.* 23: 229-230, 281-285 (1942)

²⁴⁸ A. Meller, *Paper Trade J.* 125, No. 11: 125-128 (Sept. 11, 1947)

20% pentosans for hardwood sulfate.²⁴⁹ More important, however, is the fact that the pentosans in softwood sulfite are in a form where they are more easily removed than the pentosans in either hardwood sulfite or the pentosans in sulfate pulps of either softwood or hardwood origin. Cooking by the sulfite process apparently weakens the association between the "true" cellulose and the non-cellulosic carbohydrates and renders the latter more soluble in alkali.

Sulfite pulps are generally refined by the hot process, the alkali being applied between the chlorination and hypochlorite stages of bleaching. Sulfite pulp of rayon grade, i.e., alpha cellulose content of about 90%, can be made by treating the unbleached pulp first with chlorine, then hot dilute alkali, and then with a carefully regulated hypochlorite bleach. Further refinement with hot dilute alkali will increase the alpha cellulose content to 95%, but strong alkali is required to increase the alpha cellulose content over 95% and reduce the pentosan content to less than 1.5%.²⁵⁰

Hardwood sulfite pulps contain a more resistant pentosan fraction than softwood sulfite pulps, but they, too, can be purified by hot alkali. Beech sulfite has been used in Germany and Italy for making high alpha pulps.²⁵¹ Pulp having an alpha cellulose content of 94.5% (yield 75%) has been made in Germany from a special beech sulfite pulp by extracting with 2.5% sodium hydroxide solution at 90° C. for one hour. Pulp of 96% alpha cellulose (yield 85%) has been made by extracting with cold 10% sodium hydroxide solution for one hour.²⁵² In making these pulps, the wood is cooked with a sulfite cooking liquor containing a high concentration of free sulfur dioxide (e.g., 6.5%) but low combined (e.g., 0.85%), and the cooking period is very long, often requiring seven to eight hours to reach maximum temperature, that is, about 135° C., and an additional seven hours at maximum temperature.

Refining of Alkaline Cooked Pulps

Alkaline cooked pulps, i.e., soda and sulfate pulps, are not so well suited to alkali refining as sulfite pulps because of the higher pentosan content and, more importantly, because the pentosans in alkaline cooked pulps are in a form resistant to solution by dilute alkali. Alkaline cooking liquors exert a strong solvent action on the less resistant hexosans, but do not hydrolyze and remove sufficient of the pentosans to produce a satisfactory dissolving pulp.²⁵³ Unlike the sulfite process, it is impossible during alka-

²⁴⁹ G. A. Richter, *Ind. Eng. Chem.* 32, No. 3: 324-328 (March, 1940)

²⁵⁰ G. A. Richter, *Ind. Eng. Chem.* 33, No. 12: 1518-1528 (Dec., 1941)

²⁵¹ J. E. Atchinson, *Tappi* 33, No. 2: 20-30 (Feb., 1950)

²⁵² J. N. McGovern and G. K. Dickerman, *Paper Trade J.* 124, No. 2: 13-24 (Jan. 9, 1947)

²⁵³ G. A. Richter, *Ind. Eng. Chem.* 32, No. 3: 324-328 (March, 1940)

ine cooking to depolymerize the pentosans satisfactorily without simultaneously degrading the cellulose to an appreciable extent. Increased temperature and increased cooking time do not help materially in reducing the pentosan content of hardwood sulfate pulps.²⁵⁴

Ordinary sulfate pulps cannot be satisfactorily refined by the hot process using dilute alkali.²⁵⁵ Cold refining with strong alkali is more effective than the hot process, but this, too, is not completely satisfactory. It has been claimed²⁵⁶ that sulfate pulp containing 97% alpha cellulose can be obtained by treating the pulp with 8 to 15% sodium hydroxide, washing with 4 to 6% sodium hydroxide, soaking in 1.5 to 2.5% sodium hydroxide, and finally washing in water. However, pentosans are not completely removed from alkaline cooked pulps even in 17.5% alkali,²⁵⁷ and efforts to obtain complete removal with such strong alkali is uneconomical and results in degradation of the true cellulose.

One of the most satisfactory means of producing high alpha pulps by the alkaline cooking process is by pretreatment of the wood under acid conditions prior to cooking. This method of treatment is based upon selective hydrolysis of the cellulosans to render them soluble in the cooking liquor and in subsequent hot alkali refining liquor. Another similar method involves a treatment of the unbleached pulp with agents such as 2 to 8% chlorine (as chlorine water),^{258, 259} 0.5 to 20% mineral acids,²⁶⁰ and 10% calcium hypochlorite²⁶¹ before extracting the pulp with alkali. Libby and Tasker²⁶² describe the preparation of rayon grade pulp from maple by treating the pulp with 20% hydrochloric acid (on the pulp weight) for two hours at 90° C. and then extracting the pulp with 100% sodium hydroxide on the weight of the pulp at a consistency of 10% for two hours at 20° C., followed by a single-stage bleaching with hypochlorite. However, treatment of the unbleached pulp with acid is not as efficient as pretreatment of the wood before cooking. Treatment of the bleached pulp with acid is even less efficient, since the acid is far less selective toward the pentosans when applied to the bleached pulp than when applied to the original wood.²⁶³

Cooking certain species of wood in water alone is sufficient to depoly-

²⁵⁴ C. W. Tasker and C. E. Libby, *Paper Trade J.* 123, No. 23: 181-190 (Dec. 5, 1946)

²⁵⁵ A. Meller, *Paper Trade J.* 121, No. 13: 119-131 (Sept. 27, 1945)

²⁵⁶ W. Collings, R. Freeman, M. Roberts and W. O. Hisey, U. S. 2,385,259 (Sept. 18, 1945)

²⁵⁷ E. Correns, *Cellulosechemie* 19: 105-113 (Sept., Oct., 1941)

²⁵⁸ G. Richter, U. S. 1,816,343 (July 28, 1931)

²⁵⁹ A. Bayerl, U. S. 1,967,347 (July 24, 1934)

²⁶⁰ G. Richter, U. S. 2,036,606 (Apr. 7, 1936)

²⁶¹ G. Richter, U. S. 2,028,846 (Jan. 28, 1946)

²⁶² C. W. Tasker and C. E. Libby, *Paper Trade J.* 123, No. 23: 181-190 (Dec. 5, 1946)

²⁶³ A. Meller, *Tappi* 33, No. 5: 248-253 (May, 1950)

merize the pentosans because of the acidity developed by the liberation of organic acids.^{264, 265} Pulp having an alpha cellulose content of 94% has been made from pine in Germany by cooking the wood in water at 130 to 150° C. for two to three hours (the final pH being about 3.8), after which the wood is cooked by the sulfate process.²⁶⁶ Simmonds^{266a} recommends cooking hardwoods in water at 160 to 170° C. for 30 minutes (the pH being between 3 and 4), after which the chips can be cooked with sulfate liquor of reduced chemical content (20% total chemical, 30% sulfidity, maximum temperature 170° C., and a total cooking time of 2.5 to 3.0 hours) to produce a pulp suitable for hot alkali refining.

In the production of high alpha pulps by alkaline cooking, preheating of the wood in the presence of mineral acid is more effective than preheating in plain water. Many processes have been described.²⁶⁷⁻²⁷⁰ In the European economy, the recovery of sugars from the acid prehydrolysis for use in making alcohol and fodder yeast is an important part of these processes and explains the greater interest shown in these processes by European investigators. Most of the interest in pretreatment of wood with acids has centered about the hardwood species to be cooked by the sulfate process. Prehydrolysis is of relatively little benefit, and may even be harmful, when the pretreated wood is cooked by the sulfite process.²⁷¹

Correns²⁷² studied the effect of prehydrolysis of beech before cooking by the sulfate process and found that best results were obtained by treating with a 0.3 to 0.5% solution of hydrochloric acid. Gremler²⁷³ was able to reduce the pentosan content of sulfate pulp from eucalyptus from 18% to about 2.5% by pretreating the wood with an 0.5% solution of sulfuric acid (liquor ratio 5 to 1) at 120° C. for two and a half hours before cooking by the sulfate process. His data show that the alpha cellulose is not appreciably attacked during prehydrolysis, as indicated by the fact that the alpha cellulose content of the bleached pulp is approximately the same as the alpha cellulose content of the original wood when suitable corrections are made for pentosans in the alpha cellulose. A commercial process used in

²⁶⁴ G. Richter, U. S. 1,787,953 (Jan., 1931)

²⁶⁵ G. Richter, U. S. 1,819,002 (Aug., 1931)

²⁶⁶ J. N. McGovern and G. K. Dickerman, *Paper Trade J.* 124, No. 2: 13-24 (Jan. 9, 1947)

^{266a} F. A. Simmonds, (Report of talk by) *Tappi* 33, No. 12: 100A (Dec., 1950)

²⁶⁷ E. Correns, *Cellulosechemie* 19: 105 (1941)

²⁶⁸ L. Cornell and R. Montonna, Canadian Patent 398,573 (Aug. 12, 1941)

²⁶⁹ G. Jayme, *Papier-Fabr.* 38: 277 (1940)

²⁷⁰ P. Schorning, *Holz als Roh- und Werkstoff* 3: 273 (1940)

²⁷¹ E. Correns, *Cellulosechemie* 19: 105 (1941)

²⁷² E. Correns, *Cellulosechemie* 19: 105-113 (Sept., Oct., 1941)

²⁷³ E. Gremler, Unpublished thesis, "Suitability of Eucalyptus Globulus for Dissolving Pulp." New York State College of Forestry, Syracuse, N. Y. (1949)

Germany on pine²⁷⁴ involved a treatment of the wood with a 0.3% solution of sulfuric acid at a liquor-to-wood ratio of 4.5 to 1, at 125° C. for two to three hours, after which the wood was cooked by the sulfate process. About 19% of the wood weight was lost in prehydrolysis. The final alpha cellulose content was 92 to 94%.

Refining of Other Pulps

Practically any pulp can be purified by alkali to yield a pulp high in alpha cellulose. However, there are practical difficulties preventing the use of many pulps, and so far, sulfite pulps have been used to the greatest extent, although some sulfate pulps made from pretreated wood have been used. Joglekar²⁷⁵ was able to produce a high-grade alpha pulp from bamboo by pretreating the bamboo with a 2% solution of sulfuric acid at 110° C. for 2.5 hours, followed by a sulfate cook at 165° C. with 20% active chemical (as Na₂O).

The Northern Regional Laboratory²⁷⁶ has described a process for making an alpha pulp from rice or barley straw by the following steps:

- (1) Cooking the straw with 15% caustic soda for 2 hours at 170° C.
- (2) Removing the fine fiber fraction by screening over inclined 100-mesh wire cloth.
- (3) Three-stage bleaching with (a) chlorination, (b) extraction with 2% caustic soda on the basis of pulp at 4% consistency at 50° C. for 1 hour, and (c) final hypochlorite bleach at 4% consistency and 35 to 40° C. for 2 hours.
- (4) Final extraction with 12% caustic soda solution for 1.5 hours at 6% consistency.

This process has not been used commercially, but it illustrates the special techniques which can be utilized in making purified pulps from special sources.

²⁷⁴ J. N. McGovern and G. K. Dickerman, *Paper Trade J.* 124, No. 2: 13-24 (Jan. 9, 1947)

²⁷⁵ M. A. Joglekar, unpublished thesis, "The Suitability of Bamboo as a Raw Material for the Manufacture of Dissolving Pulp." New York State College of Forestry, Syracuse, N. Y. (Sept., 1949)

²⁷⁶ S. I. Aronovsky, G. H. Nelson and E. C. Lathrop, *Paper Ind.* 29, No. 9: 1300-1303 (Dec., 1947)

FIBER PREPARATION

Cellulose fibers must be subjected to mechanical treatment before they can be made into paper. This treatment may be applied in a number of different ways, but it ordinarily includes a bruising, rubbing, or crushing action on the fibers. Certain pulps will develop some strength by simply agitating at high speeds with a stirrer, but most pulps require a more vigorous action.

The terms "beating" and "refining" are used in the paper industry to describe the operation of mechanically treating pulp fibers. Refining usually refers to a fiber separation and fiber cutting, whereas beating action may include these two effects, and also a fibrillating or bruising effect on the fiber. Sometimes, however, beating is referred to as refining in a general way, as it is one step in the refining of the pulp for paper.

Beating is probably the most fundamentally important process in papermaking. Paper made from unbeaten stock is low in strength, fluffy, porous, and unfit for most uses, whereas paper made from beaten stock is strong, dense, and hard in texture. Well-beaten fibers can be readily formed into a uniform sheet of paper of quite high density, whereas unbeaten fibers cannot. The old maxim, "Paper is made in the beater," is still as basically true today as it was over two hundred years ago. In fact, the original Hollander beater has undergone very few improvements since its development in the eighteenth century.

It is now believed that no major chemical changes in the fiber occur during beating, since the x-ray diffraction pattern is not changed. The principal effects of beating are physical, and among the most important are the following: fracture and partial removal of the primary wall of the fiber, decrease in fiber length, increase in fiber flexibility, formation of fibrils (fibrillation), and increase in the external specific surface of the fiber.

Beating, or refining, is an important step in the processing of pulp for nearly all grades of paper. For writing papers, the stock must be well beaten to produce a hard, "rattly" paper. For printed papers, the fibers should be well fibrillated and shortened to secure a smooth, close formation, although too much beating is not good for printing papers. In the case of

paperboards where maximum folding qualities are desired, it is sometimes necessary to reduce the amount of beating and sacrifice some printing qualities in order to maintain long, flexible fibers. The rate of beating is an important consideration on such grades as glassine, tracing, manifold, and greaseproof papers, where the pulp is usually beaten to nearly its maximum, and hence, easy beating pulps are desired for these grades. Fries¹ lists two important requirements of an easy beating pulp: viz., it should reach its maximum bursting strength in a short time, and it should show only a slight drop in tear and burst after it reaches its maximum.

Use of Beaters

The beater has a number of functions: it can beat or fibrillate the stock; it can be used to cut the fibers; or it can be used for mixing and blending the stock and the non-fibrous materials. The beater is sometimes used as a washing device and as a bleacher. However, the action of the beater is primarily of a rubbing or crushing nature whereby the fibers are subjected to a succession of hammer-like blows or impacts.

Variables in Beating

Dull beater roll bars, high consistency of stock, and low temperature favor this rubbing or brushing action. On the other hand, if the consistency is low, the knives sharp, and the beater roll is put down hard on the bed-plate, the action becomes predominantly of a cutting nature. In general, beaters with dull bars produce papers with higher bursting, tensile, and tearing strengths than beaters with sharp bars. Special beater rolls made of basalt lava can be used to produce a high degree of bruising action and are frequently used for the beating of pulp for glassine.

As the beater roll revolves, fibers collect on the edge of each roll bar. The thickness of this fiber mass, which Smith² calls fibrage, depends upon the length of the fibers, the consistency of the stock, the depth of bars, the spacing between bars, and the speed of circulation. The roll bars must be spaced properly to carry only the amount of fiber on which useful work can be done. On the other hand, spacing must be adequate to permit the collection of fibrage on the roll bars. For short fibers, such as wood and esparto, Tait³ recommends a spacing of $\frac{5}{8}$ in., whereas a spacing of about $1\frac{1}{2}$ in. may be necessary with long rag fibers. In most beaters, the bed-plate bars are set at an angle of from 3 to 8° to the roll bars.

¹ K. W. Fries, *Paper Trade J.* 112, No. 21: 223-224 (May 23, 1946)

² Sigurd Smith, *The Action of the Beater*, p. 36, 1923. Trans. by R. Marx, London. Tech. Assoc. of the Paper Makers' Assoc. Gt. Britain Ireland.

³ W. Tait, *Paper-Maker* 117, No. 4: 272-277, (Apr., 1949)

The effectiveness of the beater depends on a number of factors, many of which are not well understood in spite of the great number of years this machine has been in use. It is a known fact that the amount of beating is directly related to the amount of work done on the fibers. The energy that is absorbed by the stock during beating appears partly in the form of sensible heat, but according to Strachan,⁴ a large part of the power is absorbed by the cellulose during fibrillation and appears as an increase in the electrical surface charges on the beaten fibers. The power required in conventional beating is generally between 200 to 1,000 kw.-hr. per ton of finished paper.

Inch Cuts per Minute and Area of Bars

As mentioned above, the fibers collected on the beater roll are subjected to a predominantly cutting action, if the roll bars are sharp, and to a predominantly bruising or mashing action, if the bars are dull. An indication of the cutting action of the beater can be obtained by computing the inch cuts per minute, whereas the bruising or "wetting" action of the beater is indicated by the total area of the roll and bedplate bars.⁵⁻⁷

The number of inch cuts per minute can be computed by first multiplying the face of the roll in inches by the number of the roll bars, and then multiplying this by the number of bedplate bars, and finally by the number of revolutions per minute. The area of the roll and bedplate bars can be readily calculated from the thickness of the roll and bedplate bars, the number of bars, and the width of the roll.

Beating Pressure

Although inch cuts per minute and total beating area are indicative of the type of beating action, they do not give the complete picture, since they do not take into account the pressure exerted by the roll bars on the bedplate bars, which is a highly important factor. Beating pressure is generally controlled by raising or lowering the heavy beater roll bar to a predetermined position, but this does not accurately establish beating pressure, because beating pressure is also affected by the total beating area and by the consistency of the stock. For example, Tait⁶ points out that the maximum beating pressure varied from 238 p.s.i. to 380 p.s.i. when attempts were made to change the ratio of beating area to inch cuts per minute by changing the thickness of the bars. In one patented multiplate (Jones-Bertrams) beater, a counterbalanced roll is used, and this roll is actuated by a pneumatic pressure control system which controls the beating pressure in

⁴ J. Strachan, *Paper-Maker*, Midsummer Number, 6, 7, 21 (1948)

⁵ F. M. Dietz, *Paper Trade J.* 104, No. 8: 96-98 (Feb. 25, 1937)

⁶ W. Tait, *Paper-Maker* 117, No. 4: 272-277 (Apr., 1949)

⁷ Sigurd Smith, *The Action of the Beater*, p. 36, 1923. Trans. by R. Marx, London. Tech. Assoc. of the Paper Makers' Assoc. Gt. Britain Ireland.

predetermined time-pressure cycle. Means for measuring and controlling beater roll pressure can also be installed on conventional Hollander type beaters. One method uses a load element which supports one end of the front lighter bar and records and controls the pressure being exerted on the stock as it passes between the roll and the bedplate. In general, increasing roll pressure increases the refining capacity and reduces power consumption for a given strength development.⁸ Walseth and Geijer⁸ found in the beating of unbleached southern kraft with the Jones-Bertrams beater that a roll load of 125% could be used with no loss in strength and with an appreciable increase in refining capacity and a decrease in power consumption over that obtained at regular loads.

A recent development has been the introduction of an experimental multiroll beater-refiner in which three beater rolls operate against separate bedplates.⁹ Unlike the conventional beater, control is maintained through pressure adjustment of the bedplates which can apply pressures from 0 to 100 p.s.i. This beater is designed to operate continuously, rather than in a batch process, the stock being introduced through flow spreaders in front of the first beater roll.

Use of Refiners

A number of new machines have been developed to replace or supplement the beater. Within recent years, the beater has been replaced to a large extent in the high production mills by more efficient refining equipment. However, the beater is still used in the smaller mills when flexibility in fiber treatment is necessary.

Pulpers

In the past the papermaker tried to perform a number of different functions with the beater and, as a result, did none of them very efficiently. Because of this, the trend in stock preparation in recent years has been toward the replacement of the beater with several different units which perform individual functions more efficiently. Waste paper mills have for many years used a special beater known as a breaker beater which, in reality, is not a beater at all, but rather a defibering machine which breaks up waste paper and screens it through a perforated backfall. Machines called pulpers are also sometimes used for breaking up or pulping broke, waste papers, or lap pulp with a minimum of damage to the fiber.¹⁰ One of these machines* consists of a large open-top tub equipped with a high-speed rotating blade in the bottom of the tub which churns and breaks up the stock.

⁸ C. S. Walseth and C. G. Geijer, *Tappi* 33, No. 10: 490-494 (Oct., 1950)

⁹ M. R. Roberts, *Tappi* 33, No. 6: 286-288 (June, 1950)

¹⁰ R. F. Vokes, *Paper Mill News*: 30-31 (May 25, 1946)

* The Hydrapulper sold by Dilts Machine Company, Fulton, New York.

Conical Refiners

Many new refining machines have been developed in recent years, and these have been well described in the literature.¹¹ Disk refiners,^{12,13} Kollergangs (particularly in Sweden), ball mills, roller mills (Haug), and impact mills are among the types which have been suggested, but over the years the most successful has been a conical refiner known as the jordan. In this refiner, the stock enters the small end and then passes through between the rotor (plug) and the casing, both of which are equipped with metal bars, until it emerges at the large end under a head created by the rotating plug.

The jordan is used primarily for cutting, but it can also be made to do considerable "beating" if the bars on the rotor and casing are wide and the rotational speed is high. In high production mills making newsprint and kraft wrapping papers, the jordan has almost completely replaced the beater. The consistency used in jordan refining is usually somewhat less than that used in the beater, and this promotes cutting action.

Within recent years other conical high-speed refiners have replaced the jordan, particularly where a high degree of beating is desired. The interest of papermakers was first displayed in machines which were simply high-speed jordans and were called "refiners." They had a speed of from 800 to 1200 r.p.m., whereas the standard jordan turned at about 350 r.p.m. Also, the bars in both the plug and shell were wider than the normal jordan bar. The newer refining machines* differ from the jordan in design and speed of rotation and consequently have a different action on the fibers than either beaters or jordans. There is less fiber cutting and less brooming and bruising of the fiber, but more longitudinal splitting of the fiber.¹⁴ One of these refiners may take the place of two to five beaters.¹⁵ Ordinarily these machines are used in high production mills, but they have even been used for the beating of rag stock for high-grade rag content papers, where it is claimed¹⁶ that they produce pulps of greater freeness and fiber length than regular beater-treated stock. These refiners can be used effectively for refining up to the maximum tear development.¹⁷ For further strength development beyond that point, jordans are more efficient in terms of power

¹¹ *Paper Mill News*, Stock Preparation Number (May 25, 1946)

¹² D. M. Sutherland, *Paper Trade J.* 123, No. 3: 25-29 (July 18, 1946)

¹³ D. M. Sutherland, *Paper Mill News*: 12-19 (July 6, 1946)

* The Hydrafiner sold by the Dilts Machine Company, Fulton, New York.

¹⁴ F. S. Macdonald, *A Stock Preparation System*, Alexander Fleck, Ltd. Ottawa, Ontario, Canada

¹⁵ E. M. Root, "Stock Preparation. The Hydrafiner versus the Beater." Dilts Machine Co., Fulton, N. Y. (Oct. 8, 1940)

¹⁶ H. P. Espenmiller, *Paper Trade J.* 127, No. 8: 358-362 (Aug. 19, 1948)

¹⁷ F. T. Peterson, *World's Paper Trade Rev.* 133, No. 5: TS 9-19 (Feb. 2, 1950)

required per unit of strength development. Recently, conical refiners have been equipped with automatic controls for adjusting the plug of the refiner in or out to hold a predetermined power setting¹⁸ or a predetermined plug pressure.¹⁹ This results in some saving in power and also maintains more uniform fiber treatment.

Disk Refiners

Recently papermakers have shown an accelerated interest in other continuous refining machines in addition to the jordan and high-speed conical refiners which have been widely accepted. Among the most promising of the newer types are the disk refiners (Sutherland, Voith, Sprout-Waldron, and Bauer) in which refining is accomplished by passing the stock between grooved plates located on two disks. These refiners are being used to a considerable extent in mills making bag, wrapping, kraft boards, and similar grades, and to a lesser extent in high-grade mills. The units may be of the single rotation type (with one stationary and one rotating disk) or the double rotation type. Interchangeable plates in a wide variety of groove, tooth pattern, and dimension are available for attachment to the disks.

Disk refiners are used to an increasing extent for defiberizing cooked or only semicooked wood. In this treatment, the refiner complements, or even completely replaces, the cooking process. The action of the refiners in these processes is not to be compared with that taking place in conventional beating or refining, since it is primarily a defiberizing action, whereas true beating of thoroughly cooked pulp is a complex process involving colloid phenomena. Disk refining of semichemical and whole wood fibers was discussed in Chapter IV.

In addition to the use of disk refiners on raw-cooked and semichemical pulps, this type of refiner is also used (1) for reducing the size of screenings and (2) in stock preparation for strength development. In comparison to a beater or conical refiner, disk refiners do less cutting of the fibers.²⁰

Batch versus Continuous Refining

Originally, papermaking was a batch process, but after the invention of the paper machine, it became continuous. Even so, stock preparation remained a batch operation and is still so today in those mills where the beater is used. Batch refining is still retained in many mills because of the operating advantages. It is quite likely that batch refining methods will be retained in those mills making small orders of speciality high-grade papers

¹⁸ R. B. Fowler, *Paper Mill News* 73, No. 20: 64-66 (May 20, 1950)

¹⁹ B. E. Prevost, *Paper Mill News* 73, No. 20: 69-70, 72 (May 20, 1950)

²⁰ L. E. Eberhardt, *Paper Trade J.* 130, No. 25: 21-25 (June 22, 1950)

and papers which must undergo very close technical control in order to meet rigid final specifications. On the other hand, continuous refining is best suited to high production mills which make only a few different grades of paper.

Effect of Beating on Fibers

The effects of beating are of fundamental importance in determining the degree of interfiber bonding in a sheet of paper. Hence, beating is one of the most important steps determining the papermaking qualities of a given pulp. In this chapter, the subject of beating is discussed from two standpoints, the effect of beating on pulp properties and the effect of pulp properties on rate of beating. The relationship between the properties of the beaten pulp and the bonding of the fibers into a sheet of paper is discussed in the next chapter.

Because the Hollander beater has been the standard "beating" engine in the paper industry for so many years, the effects of beating are discussed in terms of this machine, but the subject has been taken up from a fundamental standpoint, so that the theory is equally applicable to all refining engines.

Effect on Sheet Properties

A chapter on beating would not be complete without mentioning the effects of beating on the final sheet properties. In general, beating improves some properties and has a bad effect on others. Thus, the papermakers must select the proper beating conditions to bring out certain properties without detracting too much from other properties. Beating must not be carried out so that any one property is emphasized too much, since this may detract from another property.

In general, increased beating within the commercial range increases bursting strength, tensile strength, and folding endurance, but generally tends to decrease tearing resistance. Increased beating tends to increase smoothness, hardness, and amount of surface bonding of the fibers, but on the other hand, tends to decrease the opacity and lower the bulk and dimensional stability of the paper.

The effect of beating on cotton pulps has been studied by Landt and Rulon,²¹ and some of their data are shown in Table I. In this work, a sample of cotton pulp, which had been cooked for eight hours in 3% sodium hydroxide, was beaten for different time intervals.

Results showing the effect of beating on the physical properties of pa-

²¹ G. E. Landt and S. A. Rulon, *Paper Trade J.* 111, No. 4: 44-48 (July 25, 1940)

per made from cotton staple fiber are shown in Figure VI-1.^{21a} Approximately the same general effects are obtained when beating wood pulp.

TABLE I

EFFECT OF BEATING ON PROPERTIES OF PAPER MADE FROM COTTON PULPS

Beating time, min.	Freeness, cc. (Williams)	Thickness, in.	Weight, g.	Area, cm. ²	Density, g./cc.	Tensile strength, lb.
30	695	0.010	8.4	870	0.38	8.50
90	205	0.0085	8.8	784	0.52	21.56
180	130	0.0075	9.0	676	0.70	29.12

Theories of Beating

Three principal theories have been proposed to explain the effects which are produced on pulp fibers during beating. These are: (1) the chemical theory, sponsored by early investigators, such as Cross and Bevan and Schwalbe, (2) the physical theory, presented in 1926 by James Strachan, and (3) the partial solubility theory, proposed by Campbell in

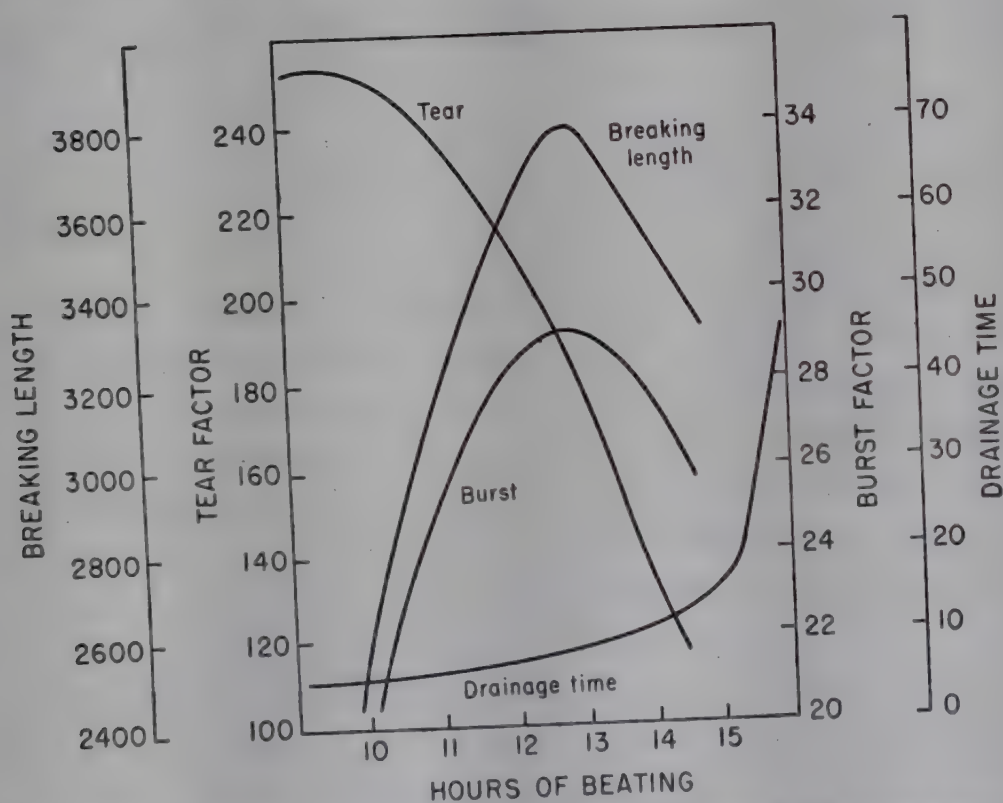


Fig. VI-1. Effect of beating on physical properties of paper made from cotton staple fiber.

1932. Since the original proposals of these theories, there have been other modifications and variations, principally those of James d'A. Clark and

^{21a} D. M. Musser and H. C. Engel, *Paper Trade J.* 113, No. 2: 13-16 (July 10, 1941)

L. G. Cottrall. The differences between Clark's, Campbell's, and Strachan's theories on beating will be brought out in the following sections on hydration and fibrillation. These theories are also discussed at greater length in the following chapter on the nature of fiber bonding.

The early chemical theory of beating has been fairly well abandoned, since it is now reasonably well proved that water does not combine chemically with cellulose in the beater and that no true hydrates are formed. Therefore, the term "hydration," which is commonly used in describing the effects obtained on beating, is a misnomer. Beating is primarily a mechanical process resulting in physical changes in the fibrous structure and colloidal nature of the pulp. No major chemical changes take place during beating, although minor chemical changes may occur as a result of the great increase in surface activity of the fiber and other changes in the

TABLE II

EFFECT OF BEATING ON CHEMICAL PROPERTIES OF UNBLEACHED MITSCHERLICH PULP

Time of beating, min.	Freeness (S-R)	Alpha cellulose	Copper number	Alkali solubility	Cuprammonium viscosity	Hydrolysis number
0	840	84.62	2.58	12.60	88	15.3
80	370	83.78	2.75	13.10	83	21.8
160	170	84.05	2.60	14.35	77	24.8
240	80	84.88	2.66	13.80	74	28.0

physical properties of the fiber.^{22, 23} Kress and Bialkowsky²² found that the alpha cellulose content, copper number, and alkali solubility all remain practically constant during the beating of an unbleached Mitscherlich sulfite pulp, as shown in Table II, whereas the cuprammonium viscosity decreases and the ease of hydrolysis of the fibers in acid increases. The increase in hydrolysis number and decrease in cuprammonium viscosity are probably physical rather than chemical effects resulting from an increase in surface activity which renders the cellulose more susceptible to chemical. Curran and coworkers²³ found, in the case of sulfate pulp, that the 1% alkali solubility was increased from 4.5 to 5.8 on beating six hours, but this, too, they attributed to a slight increase in reactive surface. A few investigators have expressed the theory that some of the main lateral bonds between the cellulose chains or micelles are broken during beating, but this is unlikely.

²² O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 219-228 (Nov. 12, 1931)

²³ C. E. Curran, F. A. Simmonds and H. M. Chang, *Ind. Eng. Chem.* 23, No. 1: 104-108 (Jan., 1931)

Swelling of Pulp Fibers

Before taking up the other effects of beating, it is desirable to discuss fiber swelling, since the phenomena which take place in beating are closely associated with the important phenomenon of fiber swelling. Dry fibers vary considerably in stiffness, depending upon the type of fiber, but all dry fibers tend to be brittle. Water-soaked fibers, on the other hand, are very flexible because they have taken up water and are swollen, which makes the individual fibers soft and pliable, increases their elasticity and plasticity, and decreases their stiffness. This increase in flexibility is desirable, since it prevents severe breakage of the fibers during beating, which would occur if beating were started before the fibers had swollen. Moreover, the increase in fiber pliability furthers the fibrillation of the pulp, which increases the bonding area in the sheet and thereby increases the density and strength of the final paper. Strachan²⁴ reports that certain fibers on beating may swell to twice their dry diameter.

Swelling proceeds fairly rapidly for most fibers, but there is some difference between fibers which have soaked in water for a long time and those which have soaked for only a few minutes. This difference in soaking time is important in many cases where it means that water has entered the fiber, changing it from a ribbon to a cylinder. When "wet" beating is desired, the beating is carried out slowly to allow ample time for water to penetrate the fiber and make it plastic. On the other hand, when a "free" stock is desired, the beater roll is set down quickly to cut the fibers before too much swelling occurs and while the fibers are still brittle and easily cut. Low temperature favors the swelling of pulp fibers in water.

Chemical wood fibers, as a rule, become highly flexible on slight refining, but this depends to some extent upon the type of fiber, since fibers which are heavily encrusted with lignin are less flexible than bleached fibers, and summerwood fibers tend to be less flexible than the springwood fibers from the same pulp. Since pentosans swell in water more than cellulose, a high pentosan content would be expected to increase the flexibility of wet fibers (although the reverse is true after the fibers are dried). Young and Rowland²⁵ noted a nearly linear relationship between swelling and pentosan content in the case of softwood pulps, as shown below in Table III, but not in the case of hardwood pulps. The results of Robertson and Mason²⁶ indicate that there is a relationship between fiber swelling during beating and the strength properties of sheets made from the pulp.

²⁴ J. Strachan, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain, Ireland* (March, 1926)

²⁵ G. H. Young and B. W. Rowland, *Paper Trade J.* 97, No. 15: 44-46 (Oct. 12, 1933)

²⁶ A. A. Robertson and J. G. Mason, *Pulp Paper Mag. Canada* 50, No. 13: 103-110 (Dec., 1949)

Groundwood fibers retain their stiffness longer on beating than most fibers because of their greater lignin content and consequently cannot take much beating without excessive fracturing of the fibers.

Pulp fibers take up water by both porous imbibition and capillary absorption. In porous imbibition, the water is taken up in preformed cavities such as the pits, pores, and lumen of the fiber, the mere filling of which with water does not change the dimensions of the fiber. A somewhat different condition exists when the water enters the small, submicroscopic pores of the fiber where the processes of imbibition and swelling overlap. Absorption of water in this way loosens the fibrils, making it easier for them to

TABLE III

RELATION BETWEEN PENTOSAN CONTENT AND SWELLING OF SOFTWOOD PULP FIBERS

Pulp	Pentosan content, %	Increase in volume on swelling, %
No. 1 alpha	2.4	42.0
Bleached sulfite	4.5	54.0
Bleached sulfite	4.7	57.0
Bleached sulfite	6.7	57.5
Unbleached sulfite	6.9	58.0
Unbleached Mitscherlich	6.9	60.5
Unbleached sulfite	7.4	57.5
Bleached Swedish kraft	10.8	63.5
Unbleached kraft	10.9	79.0
Groundwood (spruce)	11.6	87.5
Bleached sulfite	11.7	93.0
Southern kraft	12.6	96.0

separate on beating. As the fiber swells, more spaces are opened up and additional water enters the fiber. However, true inter-crystalline swelling does not occur, since water is not a strong enough swelling agent to pry apart the cellulose crystallites.

The ability of pulp fibers to swell is attributed to their hydroxyl groups,²⁷ since without these polar hydroxyl groups, cellulose fibers will not swell in polar liquids. Kress and Bialkowsky²⁸ measured the swelling of cellulose fibers in various liquids and found that highly polar liquids such as water, formamide, and ethylene glycol result in considerable swelling, whereas non-polar liquids result in very little, if any, swelling. Thus, water and ethylene glycol result in a 90% increase in volume, and formamide in a 125% increase in volume, whereas *n*-propyl alcohol results in only a 6%

²⁷ A. R. Urquhart, *J. Textile Inst.* 20: T 125 (1929)

²⁸ O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 219-228 (Nov. 12, 1931)

increase and fuel oil in only a 2% increase in volume. The swelling power of alcohols decreases as the length of the hydrocarbon chain increases. Only those liquids which show a high swelling tendency toward cellulose permit separation of the fibrils on beating.

Effect on Primary Wall

Covering the outside of the natural fiber is a layer known as the primary wall. This layer is permeable to water, but does not swell appreciably in water, which makes it a deterrent to fiber swelling and fiber bonding. In most cases, the primary wall is partially removed from wood pulp fibers by the time the pulp reaches the paper mill, inasmuch as cooking, bleaching, and washing tend to remove it.²⁹ In new unbleached cotton cuttings, the primary wall may still be present, but since most cotton rags have been bleached before they reach the paper mill, the primary wall is pretty well removed.

In some cases delignified wood fibers, which contain all the attributes of an easy-beating pulp, i.e., low lignin content and high hemicellulose content, may be slow to beat because of the tenacious outer layer of the fiber which resists the effects of beating.³⁰ Many chemists have pointed out that without extensive beating there is enough of the primary wall left on the surface of commercial pulps to prevent the maximum adhesion of the fibers. However, beating tends to break up and rub off whatever part of this wall which is left, thus exposing the layers of the secondary wall which swells very greatly. The considerable rate of increase of sheet strength which normally occurs in the early stages of beating can be attributed to the removal of the primary wall.²⁹ When this occurs, the secondary wall is no longer constricted and can swell to two to three times its original diameter.³¹

Hydration of Pulp

Water of hydration, in the strict chemical sense, means water which is combined in definite molecular proportions and forms part of the structure of a substance. This water can be removed by changing the temperature and vapor pressures of the compound and its surrounding medium, but the vapor pressure curve shows definite breaks, and the material changes in physical properties as water is removed. The term "water of hydration" is sometimes used in reference to water held as ions in a loosely bound enveloping film. In a strict sense, this is not water of hydration, since the water bound in this way is continuously variable with changes in tempera-

²⁹ J. d'A. Clark, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 24: 30-54 (Dec., 1943)

³⁰ E. Hägglund and B. Webjorn, *Svensk Papperstidn.* 52, No. 6: 131-137 (Mar. 31, 1949)

³¹ H. F. Lewis, *Tappi* 33, No. 8: 418-424 (Aug., 1950)

ture and other conditions and has none of the absolute definiteness of the crystalline hydrates. Water held by capillary condensation is not the same as true water of hydration, even though it is usually strongly held, since it does not affect the chemical properties of the material with which it is associated.

Cellulose probably does not contain water of hydration in the true chemical sense, even though it does attract and intimately hold water molecules. Most chemists now believe that the water held by cellulose forms no part of the cellulose crystal structure, but rather is held at the hydroxyl groups on the surface of the cellulose crystallites by a special type of secondary valence force known as hydrogen bonding. It is true that this water is so strongly held that some volume contraction of the molecules is brought about,³² but the water lies between the cellulose crystallites and not within them. It is only in this sense that cellulose is hydrated.

In spite of the fact that cellulose does not form a true hydrate, it is obvious to anyone familiar with papermaking that a highly beaten pulp "binds" more water than an unbeaten pulp, and that part of this water is rather strongly held by the fibers. However, this water is considered by most chemists to be physically held water and not water of hydration. Bell³³ substantiated this viewpoint by showing that the difference in the amount of water retained by pulps beaten for different periods of time is not appreciable, if the pulps are allowed to come to equilibrium under pressure. However, it required as long as fourteen days under 200 lb. pressure for equilibrium to be reached in a highly beaten pulp, or, as Jahn and coworkers³⁴ found, a pressure of 3,000 p.s.i. for four hours. They found that the amount of water retained by laboratory test sheets (made on the standard sheet machine) immediately after couching, but without pressing, is a good indication of the changes brought about by beating.

The work of Campbell and coworkers has been particularly enlightening on the cellulose-water relationship during beating. Their work has shown that beating causes relatively little change in the amount of water absorbed on the surface of the cellulose crystallites. This conclusion is logical, since it is now known that the interior surfaces of the cellulose crystallites, even in unbeaten fibers, are readily accessible to water molecules, and hence the only means by which the amount of adsorbed water could be increased is by fracturing the crystallites, which does not take place to any appreciable extent during beating. In other words, the fibers reach equilibrium moisture content after a relatively short soaking period and no

³² W. B. Campbell, *Paper Trade J.* 95, No. 8: 81-86 (Aug. 25, 1932)

³³ J. H. B. Bell, *J. Soc. Chem. Ind.* 52: 109-139 (1933)

³⁴ A. Sedoff, C. V. Holmberg and E. C. Jahn, *Paper Trade J.* 109, No. 26: 350-357 (Dec. 28, 1939)

further "hydration" takes place on beating. In carrying out their experiments, Campbell and coworkers³⁵ made a series of determinations of water vapor pressures of unbeaten and beaten pulps at various moisture contents. They found that the sorption isotherms were continuous, and that there was only a small increase (ratio of 1.05 to 1.00 for beaten to unbeaten pulp) in the amount of water adsorbed by beaten pulps, and from this concluded that the effects of beating were purely physical. Seborg, Simmonds, and Baird³⁶ also carried out a series of sorption experiments, and they found that pulps beaten to an extreme degree sorb from 0.2 to 3.5% more moisture than unbeaten pulps, depending on the relative humidity. They attributed this to a slight increase in number of free hydroxyl groups made available for the adsorption of water vapor. Argue and Maass³⁷ found that the heat of wetting was increased from 2% to 10% as a result of beating, which they attributed to a slight increase in the internal surface of the fibers. McGregor³⁸ found, on the basis of freezing point lowering with sucrose, that all the water in the pulp-water system is in a "free" state and not bound with the cellulose.

It is now pretty well agreed that the changes which take place during beating are not due to chemical hydration or capillary imbibition of water, but are the result of a combination of physical changes which must be termed "papermakers' hydration." Thus the term "hydration" as used in the paper industry is confusing, since it must be given an empirical interpretation. Many chemists have dropped the term "hydration" in favor of the term "wetness," which is less confusing. Pulp is fully hydrated in the usual sense of the word before it is beaten, but beating does increase the wetness or tenacity with which the fibers hold water, and in this way affects the rate of drainage on the paper machine wire. The amount of wetness which is developed in the beater is a very important factor in determining the properties of the final paper. It affects the amount of fiber-to-fiber bonding, and hence, the bursting and tensile strengths of the paper, as well as the stiffness, porosity, opacity, etc.

Fibrillation

An important effect of beating is the fraying out or fibrillation of the fibers. In 1926, Strachan³⁹ attacked the chemical theory of beating and

³⁵ J. K. Russell, O. Maass and W. B. Campbell, *Can. J. Research* 15, Sec. B, No. 1: 13-18 (Jan., 1937)

³⁶ C. O. Seborg, F. A. Simmonds and P. K. Baird, *Ind. Eng. Chem.* 28, No. 11: 1245-1250 (Nov., 1936)

³⁷ G. H. Argue and O. Maass, *Can. J. Research* 12: 564-574 (1935)

³⁸ G. H. McGregor, *Paper Trade J.* 93, No. 7: 65-68 (Aug. 13, 1931)

³⁹ J. Strachan, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland*, Sec. 6, p. 139 (1926)

established the basis for the present theory of fibrillation. According to Strachan's ideas, the so-called hydration obtained on beating is really fibrillation of the fiber surfaces which increases the specific surface and the amount of water imbibed.

Before the phenomenon of fibrillation can be explained, it is necessary to understand the structure of cellulose fibers. This has already been discussed in Chapter I, and it is sufficient to point out here that fibers are composed of individual cellulose molecules which are associated into crystallites, which in turn are associated into thread-like fibrils. The fibrils, which are relatively coarse morphological units, are plainly visible in the electron microscope, and are also visible under the optical microscope when silvered by a special technique. Most chemists also recognize the existence of still smaller units called sub-fibrils or fibrillae, which are conceived as extremely fine units composed of fine crystallites or individual cellulose molecules. The fibrillae are for the most part visible in the electron microscope,⁴⁰ although they probably range in size down to units which are invisible.

Fibrillation involves a loosening of the coarse fibrils and a raising of fine fibrillae on the surface of the fibrils.⁴⁰ Strachan originally visualized the beating process as the development of a fine "pile" of fibrillae on the surface of the fiber somewhat analogous to the pile on velvet with the effects being largely confined to the surface of the fiber where they produce a tremendous increase in the external specific surface.⁴¹ The presence of this fine fuzz-like material accounts for the tremendously large surface of beaten fibers. Beating increases the external surface of the fibers at the expense of the internal surface, but does not affect the total surface.

Most chemists now recognize the importance of fibrillation, but there has been considerable disagreement regarding the dimensions of the fibrils which are produced. Strachan⁴² observed the presence of fibrils when examining the surface of relatively unbeaten fibers with the ordinary microscope and assumed that they were bundles of microfibrils about 0.2 micron in diameter. Electron micrographs of a positive replica of ordinary paper taken at a magnification of $6,200\times$ show the presence of fibrils 0.05 micron in width and even smaller.⁴³ Sears,⁴⁴ in his work with the electron microscope, observed the presence of very fine fibrils which he estimated to be

⁴⁰ J. d'A. Clark, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 24: 30-54 (Dec., 1943)

⁴¹ J. Strachan, *Paper-Maker* TS 13-14 (Feb., 1946)

⁴² J. Strachan, *Paper-Maker* TS 1-2 (Jan., 1946)

⁴³ T. G. Rochow, G. E. Coven and E. G. Daris, *Paper Trade J.* 126, No. 9: 104-109 (Feb. 26, 1948)

⁴⁴ G. R. Sears and E. A. Kregel, *Paper Trade J.* 114, No. 12: 139-145 (Mar. 19, 1942)

50 millimicrons (500 Å.) or less in width. Clark⁴⁵ postulates that beaten fibers are covered with a fine fuzz of micellae from 50 to 100 Å. in width, and that these in turn are probably covered with a yet finer fuzz of molecular dimensions. He believes that the fine fuzz is cemented to the body of the fiber on drying and does not reappear on wetting, unless the pulp is again beaten.

The phenomenon of beating may be explained by the fibrillation theory somewhat as follows. First, the fibers imbibe water and swell, which results in a weakening of the cohesive forces. In this wet swollen condition, the fibers are low in strength and very soft and plastic so that the mechanical action of the beater tends to loosen the individual fibrils. At the same time, still finer fuzz-like material, which may consist of individual cellulose molecules or fine crystallites, is raised on the surface of the fibrils. The loosening of fibrils within the fibers (internal fibrillation) increases the flexibility of the fibers so that they can be more easily pressed into contact during sheet formation, and the raising of fibrillae on the fiber surface (external fibrillation) increases the amount of surface available for contact. These two actions tremendously increase the external specific surface of the fiber and the amount of water which is retained in the fiber network. When the fibers are formed into paper, the fibrillae and smaller units entangle to form a sheet of high strength and density. The fibrillae also contribute to the retention of fillers in the paper by reducing the pores in the wet fibrous mat and entrapping the fine particles.

Under ordinary papermaking conditions, the only method of obtaining a sheet with a high solid fraction is through fibrillation. Some chemists have pointed out that the major strength increase obtained on beating occurs in some cases before fibrillation begins, but by this is meant only the coarse fibrillation which is easily visible under the optical microscope, and not the submicroscopic loosening of the fibrillae which precedes this effect. The work of Doughty⁴⁶ indicates that very little beating is necessary to develop the surface effects required for good bonding of the fibers but, as he points out, very high pressures are required for forming the sheet compared to the much lower pressures required for more highly beaten pulp. Furthermore, even under mild conditions of beating used in these experiments, there is probably some fibrillae raised on the surface of the fibers.

Fibrillation takes place as a result of the mechanical pounding of the fibers by the beater roll. Strachan has presented an electronic theory to explain fibrillation in which the displacement of each fibril on the surface of the fiber requires a definite expenditure of energy, and the amount of this energy is dependent on the magnitude of the forces holding the cellulose

⁴⁵ J. d'A. Clark, *Pulp Paper Mag. Canada* 44, No. 2: 91-102 (Feb., 1943)

⁴⁶ R. H. Doughty, *Paper Trade J.* 95, No. 1: 4-11 (July 2, 1932)

crystallites together.^{47,48} The type of fibrillation can be controlled by the beating process. External fibrillation, which tends to produce strong, opaque papers, is favored by prolonged light beating. Internal fibrillation, which tends to produce strong, relatively translucent papers, is favored by hard beating. Thus, the type of refining equipment is important, e.g., fibers treated in a pebble mill are generally more highly fibrillated than those treated in a beater.

Various pulps differ in the type and amount of fibrillation which they undergo on beating. Jute, for example, shows no visible fibrillation in the ordinary optical microscope, but this does not mean that none occurs, since

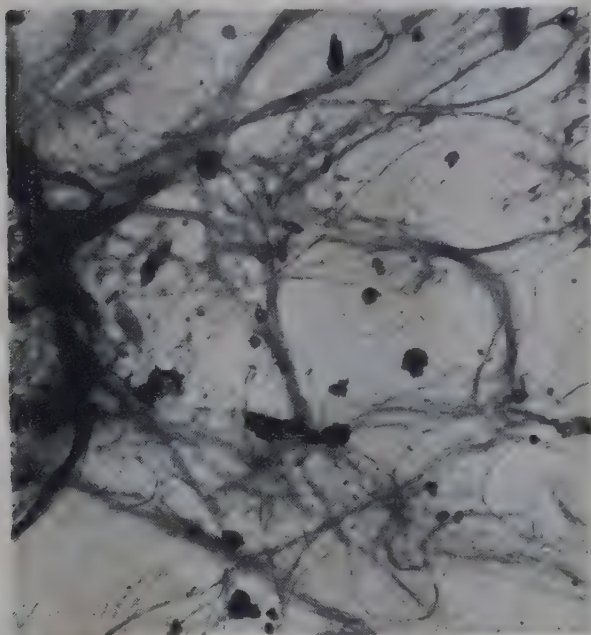


Fig. VI-2a. Disintegrated kraft pulp (8500 \times). Courtesy Stamford Research Laboratories, American Cyanamid Company.



Fig. VI-2b. Disintegrated cotton fibers (8500 \times). Courtesy Stamford Research Laboratories, American Cyanamid Company.

submicroscopic fibrillation is still likely. Linen and hemp fibers, when properly beaten, tend to split lengthwise and unravel into a mass of fine thread-like fibrils, whereas cotton staple fibers unravel in a spiral direction. Most observations have been restricted by the limitations of the optical microscope, but with the aid of the newer electron microscope, it will be possible to make more significant observations. Remarkably clear photographs of beaten kraft and cotton pulps taken with the electron microscope are shown in Figures VI-2a and VI-2b.

Wood fibers often show very little fibrillation that is visible under the optical microscope without silvering unless the fibers are well beaten. How-

⁴⁷ J. Strachan, *Paper-Maker* 110, No. 5: TS 37-38 (Nov., 1945)

⁴⁸ J. Strachan, *Paper-Maker* 113, No. 6: 33-34 (June, 1947)

ever, even though there is no visible fibrillation, Seifriz and Hock⁴⁹ have shown by means of microdissection experiments that beaten fibers separate more easily into fibrils than unbeaten fibers because of their internal fibrillation. During the fibrillation of wood fibers, the outer layer of the fiber unravels spirally, while the inner layers split in a longitudinal direction. All wood fibers do not fibrillate to the same extent. For example, softwood fibers tend to fibrillate to a greater extent than hardwood fibers, and in fact, the latter may show little or no visible fibrillation when cooked by the soda process. Normally, springwood fibers are more readily fibrillated (and also more easily cut and broken) during beating than summerwood fibers. An interesting recent observation has been that cellulose fibers which have been oxidized with periodate to produce a high percentage of carbonyl groups in the cellulose molecule do not fibrillate in the normal manner.⁵⁰

Fiber Cutting

Another effect which takes place in the beater is a cutting of the fibers into shorter lengths. The beating process may thus be regarded as a means of reducing the mean effective size of the pulp fibers not only as a result of fibrillation, but also through fiber cutting.⁵¹ Sutermeister⁵² recognizes two types of cutting, that due to the shearing action of the roll bars on the bedplate bars and that due to the cutting of the fibers by one another when high pressure is exerted on stock at high consistency.

Fibrillation is desirable, but fiber cutting is ordinarily undesirable, since it is uneconomical to use long-fibered stock and attempt to shorten it by beating or refining. However, there are some cases where fiber cutting is necessary, for example, with rag stock which is usually cut intentionally in order to reduce the average fiber length and promote a more even formation on the paper machine. In beating rag stock for blotting, filter, drawing papers, etc., it is customary to beat the stock lightly in the early stages until all the fabric is unwoven and the threads untwisted, and then set the beater to produce cutting. These are grades of paper where a short, free stock is desirable in order to obtain a bulky sheet that is well closed. Long-fibered softwood pulps may sometimes require a small amount of fiber cutting, but hardwood pulps rarely do, since they have a fiber length which is only about one-third that of spruce or hemlock.

Beating increases bursting strength of paper over most of the beating range, but as beating continues beyond a certain point, the fibers become

⁴⁹ W. Seifriz and C. W. Hock, *Paper Trade J.* 102, No. 19: 251 (May 7, 1936)

⁵⁰ M. O. Schur and R. M. Levy, *Paper Trade J.* 124, No. 20: 221-222 (May 15, 1947)

⁵¹ R. H. Doughty, *Paper Trade J.* 94, No. 9: 114-119 (Mar. 3, 1932)

⁵² E. Sutermeister, *Paper Ind.* 542-547 (July, 1947)

shorter and more mashed, and no further strength can be developed. Thus, at some point in the beating cycle, the gain in bursting strength due to fibrillation and "wetting" begins to be neutralized by the production of more and more short fibers and fiber debris, and at this point the burst test begins to decrease. The tearing strength is greatly affected by beating, and ordinarily it starts to decrease very early in the beating cycle, partly because of a shortening of the fiber, although other effects are involved (see Ch. XVI). If beating is carried far enough, the gross fiber structure is completely destroyed.

Beating or refining can be readily controlled to regulate the amount of fiber cutting. The fibers are quite susceptible to cutting, since most of the fibers in the beater pass transversely over the bar edges, thus placing them in the most favorable position for cutting.⁵³ Low consistency, high pressure between roll and bedplate, sharp tackle, and undercut wood in the bedplate are some of the conditions which favor cutting. On the other hand, "wetting" or fibrillation are favored by long beating time, low pressure, dull tackle, and high consistency (5–7%). In general, cutting is more pronounced with fibers which are stiff and brittle, and for this reason, cutting is easier in the early stages of beating before the fibers are softened by absorption of water and fibrillation. Pulps vary in the ease with which they are cut in the beaters. For example, Cottrall⁵⁴ has shown that pulps high in alpha cellulose cut more readily than pulps high in gamma cellulose. Soda pulps are much more readily cut than high-strength sulfite pulps. The type of refining engine is also very important. Jordans tend to cut more than most beaters and consequently lower the tearing strength in proportion. On the other hand, claims⁵⁵ have been made that certain attritional refiners reduce the fiber length less than beaters and hence produce papers of higher tearing strength at the same bursting strength.

In addition to its effect in fibrillating and cutting the fibers, beating also tends to create fiber debris, because of a rubbing off of fibrillated material from the surface of the fibers. Thus, beating first increases the amount of cellulosic and hemicellulosic material in a fine state of subdivision on the surface of the fibers and then rubs some of the colloidal material loose. This fiber debris is important, since it serves to fill in the voids between the larger fibers during sheet formation, thus facilitating the bonding between fibers and increasing the density, hardness, and rattle of the paper. Clark⁵⁶ has shown experimentally that a coarse suspension of fiber debris obtained by

⁵³ Sigurd Smith, *The Action of the Beater*, p. 36. Trans. by R. Marx, London. Paper Makers Assoc. Gt. Britain Ireland (1923)

⁵⁴ L. G. Cottrall, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* (Dec., 1944)

⁵⁵ R. B. Brown, *Paper Trade J.* 96, No. 23: 288–290 (June 8, 1933)

⁵⁶ J. d'A. Clark, *Pulp Paper Mag. Canada* 44, No. 2: 91–102 (Feb., 1943)

passing cellulose through a colloid mill increases the density and strength when added to ordinary pulp used in making hand sheets. Fiber debris contributes greatly to the "slowness" of the pulp, as can be illustrated by removing the major portion of the fiber debris from well-beaten pulp by washing the pulp over a 150-mesh screen. The fibers retained upon the screen will have a much higher freeness than the original stock.

Freeness

The freeness tester is an instrument which is commonly used by the paper technologist to determine the degree of beating. The freeness value is measured by the ease with which water passes through papermaking fibers while they are being formed into a wet mat on the perforated plate of the freeness tester. Freeness is therefore a measure of the rate of drainage of the pulp. A "free" pulp drains readily, whereas a "slow" pulp drains its water slowly.

The freeness tester consists of: (1) an upper container of 1-liter capacity with a perforated plate,⁵⁷ a bottom cover, a hinged top, and a petcock for the admission of air in the top cover; (2) a funnel-shaped bottom part which contains a standard orifice in the bottom and an overflow connection in the side. The water draining from the pulp in the upper container falls into the funnel and flows out the standard bottom outlet at a rate dependent upon the size of the standard orifice and the head of water upon it. If water draws into the funnel from the pulp at a rate greater than can be handled by the standard outlet, the excess flows out the side outlet and is collected in a graduated cylinder. The volume of this free water which flows out the side outlet is a function of the rate at which the water drains from the pulp suspension, and, when measured in cubic centimeters, is called the "freeness." The standard conditions used for Canadian standard freeness are 20° C. and 0.3% consistency (moisture-free pulp). Readings made under other conditions than these can be converted to standard conditions by the use of correction charts. The results depend upon the temperature and consistency of the stock and the degree of beating of the fibers. The freeness test works best on slush pulps. In some cases, freeness tests may be made upon samples of paper and dry pulp by first defibering the sample, but such samples give lower equivalent values than those obtained with the original slush pulp and are not indicative.

The freeness value decreases with increased beating, and consequently, the freeness test is used to measure and control the results of the beating process. With most pulps, the freeness decreases in a slightly S-shaped curve as the time of beating is increased. The cereal straws are exceptions,

⁵⁷ In the Schopper-Riegler tester a 60 × 80 mesh screen is used.

since they show almost a straight-line decrease in freeness with beating time.⁵⁸

There are several different freeness testers in common usage, and the approximate interconversion of results obtained on different testers is shown in Table IV. It is not possible, however, to set up absolute conversion charts, because two different samples of pulp sometimes show different relative freeness values when tested on different freeness testers.⁵⁹

During drainage of the wet sheet on the perforated plate of the freeness tester, the water must pass through the fine capillary passages which are formed between the fibers. As Campbell has pointed out, the system is subject to the laws of capillary or viscous flow, with the resistance to flow being equal to the length of the capillaries and to the fourth power of the diameter of the capillaries. The freeness value therefore measures a compound value, since it is influenced by "wetness," fibrillation, length and stiffness of fibers, surface of fibers, and the formation of the fibrous mat. The freeness value indicates how the stock will perform on the paper machine, but it gives little or no definite information about the other properties of the pulp.⁶² For one thing, the test does not distinguish between "slowness" due to short fibers and "slowness" due to fibrillation, since both reduce the average size of the passages in the wet mat. Sutermeister⁶³ believes that the total "slowness" of a pulp consisting of a mixture of long and short fibers may be due in equal part to fiber shortness and "hydration," although others^{64, 64a} believe that fiber length has no affect on freeness.

Because of its indefinite nature, the freeness value does not always correlate with the strength of the pulp. For example, Sutermeister⁶⁵ reports that the tear factor on a given kraft pulp varied from 1.5 to 2.75, even though the pulp was beaten to the same freeness value. In order to obtain more complete information on a given pulp, it is desirable to run a fiber classification according to length, in addition to the freeness test. With the results of both of these tests available, it is possible to interpret more accurately the true nature of the pulp. One difficulty is that fractionation does not work as well for beaten pulps as for unbeaten pulps.⁶⁵

Boiling of beaten fibers has been suggested as a means of measuring the slowness due to "wetness," since boiling reduces or eliminates the slowness

⁵⁸ S. I. Aronovsky, A. Rhodes and E. C. Lathrop, *Paper Trade J.* 124, No. 13: 49-54 (Mar. 27, 1947)

⁵⁹ R. W. Reed, *Paper Trade J.* 114, No. 25: 291-297 (June 18, 1942)

⁶² L. G. Cottrall, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 25: 175-181; discussion 182-198 (Dec., 1944)

⁶³ E. Sutermeister, *Paper Ind.* 29, No. 24: 542-547 (July, 1947)

⁶⁴ Talk given by K. P. Geohegan, *Tappi* 33, No. 6: 66A, 68A, 70A, 72A (June, 1950)

^{64a} J. d'A. Clark, *Paper Trade J.* 115, No. 26: 34-42 (Dec. 24, 1942)

⁶⁵ E. Sutermeister, *Paper Ind.* 29, No. 24: 542-547 (July, 1947)

TABLE IV
FREENESS SCALE INTERCONVERSION^{60, 61}

CANADIAN STANDARD 3g.-20°C.	SCHOPPER RIEGLER 2g.-20°C.	WILLIAMS PRECISION 3g.-25°C. 4g.-25°C.		MOTCHMANS SLOWNESS 1g.-20°C. Kraft Unbl. Sulphite		ORIGINAL GREEN 3g.-20°C.	WILLIAMS MODEL-27 4g.-20°C.
NOTE - This data should be used only for approximate comparisons.							
900							
		0	0				
		4	4				
800	11.5	7	7	0	0	730	855
	12.5	8	8			720	830
	13.5	10	10	15	15	705	806
	14.5	13	13	19	19	690	780
700	15.5	16	16	23	23	675	757
	16.5	18	19	27	28	660	728
	17.5	21	22	31	34	645	707
	18.6	24	25	36	39	625	680
600	20.0	27	30	41	45	610	655
	21.0	31	34	46	50	595	630
	22.5	35	39	51	56	575	607
	23.7	39	44	57	62	560	580
500	25.3	43	49	63	69	535	555
	26.7	49	56	69	75	515	530
	28.5	55	63	77	83	495	505
	30.0	61	73	85	91	470	480
400	32.0	68	80	93	100	445	457
	34.0	76	91	103	109	420	432
	36.0	85	102	114	120	395	408
	38.0	95	115	125	132	365	385
300	40.3	106	129	139	145	330	358
	43.0	120	145	153	160	305	330
	45.4	134	165	169	178	275	305
	48.3	153	195	187	197	240	282
200	51.5	173	217	206	216	210	258
	54.8	205	252	227	238	175	232
	59.0	248	297	249	257	145	210
	63.2	303	370	272	279	115	183
100	68.0	400		297	303	90	157
	73.2			322	330		
	80.0			350	364		
	90.0			390	420		

due to "wetness," but would not reduce any slowness due to fiber length.⁶⁶ Sutermeister⁶⁵ reports that soda pulps retain 80% or more of their freeness

⁶⁰ R. D. Kehoe, *Tech. Assoc. Papers* 20: 219 (1937)

⁶¹ Taken from TAPPI Data Sheets

after boiling, indicating that most of the slowness of soda pulps is due to fiber length and not to hydration. Le Compte⁶⁶ has shown that boiling of beaten Manila hemp fibers results in a reduction in "wetness," but that stirring results in a complete recovery of the lost "wetness" within thirty-five minutes.

Effect of Beating on Specific Surface

As has already been mentioned, beating loosens the fibrils and fibrillae and thereby increases the external surface of the fibers.^{67,68} There is a real need for a satisfactory method of measuring the surface created by beating and the total surface available for fiber bonding.⁶⁹ The most widely used method is one developed by Clark⁷⁰ in which a thin film of metallic silver about 0.1 micron in thickness is deposited on the fiber surfaces by boiling the fibers in ammoniacal silver nitrate, after which the area of this silver film is measured by its ability to decompose catalytically a dilute solution of hydrogen peroxide under standard conditions. This silvering technique measures only the "external" surface of the fibers and does not measure the "internal" surface, since the silver deposits are too small to enter the submicroscopic spaces between the cellulose crystallites.⁷¹ Beating increases the external specific surface as measured by this technique, but does not increase (and, in fact, actually decreases) the internal surface of the fibers. Using this silvering technique, Clark found that the fiber surface is increased in proportion to the logarithm of the amount of beating.

In addition to the silvering method, there are several other methods of measuring the specific external surface of beaten fibers. These methods may be classified as microscopic, optical, and permeability methods. Permeability methods are based upon the resistance of a uniform pad of pulp to the flow of water. Drainage resistance and freeness tests are widely used as crude empirical methods for indicating the relative surface area of beaten fibers, but more scientific methods are required for exact measurements of specific area. The Kozeny equation (derived from Poiseuille's equation) can be used for measuring specific surface based on flow of water through a pad of pulp. One form of the equation is as follows:⁷²

$$Q = \frac{1AP\epsilon^3}{fL\eta S^2(1-\epsilon)^2}$$

where Q = the volume rate of flow, cc./sec.,

⁶⁶ T. R. Le Compte, *Paper Trade J.* 93, No. 14: 156-158 (Oct. 1, 1931)

⁶⁷ O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 219-228 (Nov. 12, 1931)

⁶⁸ W. B. Campbell, Canada Dept. Interior, *Forest Service Bull.* 84, 1933, 52 pp.

⁶⁹ W. B. Campbell, *Tappi* 32, No. 6: 265-271 (June, 1949)

⁷⁰ J. d'A. Clark, *Tech. Assoc. Papers* 25: 568-575 (June, 1942)

⁷¹ L. G. Cottrall, 45th General Conference, Paper-Makers' Assoc. of Great Britain

⁷² W. B. Campbell, *Tappi* 32, No. 6: 265-271 (June, 1949)

A = the area of cross section, sq.cm.,

P = the pressure drop, cm. Hg.

L = the tube length, cm.,

η = the viscosity of the flowing liquid, poises,

f = a shape factor depending on the shape of the tube cross section,

ϵ = the void volume,

S = exposed surface area, sq. cm./g.

Since ϵ equals void fraction, $1 - \epsilon$ must equal the solid fraction and the total surface is equal to $S(1 - \epsilon)$.

By microscopic measurement, Graff and coworkers and others^{73,74} obtained values for the microscopically visible specific surface of unbeaten wood fibers ranging from about 3,600 to 5,300 cm.²/cm.³. These figures are undoubtedly low because of the method of averaging in computing areas from measured fiber dimensions. Representative values obtained by Clark,⁷⁵ using his silvering method, range from about 6,400 cm.²/g. for unbeaten southern kraft, 17,200 cm.²/g. for beaten west coast sulfite, to about 31,000 cm.²/g. for a mixture of fully beaten groundwood-sulfite stock. Using a permeability method based on the Kozeny equation, Mason⁷⁴ reports a value of 16,200 cm.²/g. for unbeaten sulfite and 100,500 cm.²/g. for the same pulp after beating for 50 minutes in a Valley laboratory beater. Campbell⁷⁶ reports values ranging from 12,960 for unbeaten pulp to 49,500 for beaten pulp. Brown⁷⁷ obtained values using a modified silvering technique of 9,300 cm.²/g. for unbeaten bleached sulfite (west coast) pulp and 10,200 cm.²/g. for the same pulp beaten.

Mason and Robertson⁷⁸ obtained the results in Table V showing the effect of beating on specific surface and effective specific volume for both sulfite and kraft pulps (undried) using the permeability method. The results show that specific surface increases regularly, whereas effective specific volume increases rapidly in the early stages of beating and subsequently levels off at a constant value. The sulfite pulp developed specific surface at a greater rate than the sulfate pulp. The effect of beating on the specific surface of a strong and a bleached sulfite pulp, as measured by the silvering technique, is shown in Table VI, taken from data of Nordman.⁷⁹ Additional results are shown in Table I in Chapter VII.

⁷³ J. H. Graff, M. A. Schlosser and E. K. Nihlen, *Tech. Assoc. Papers* 24: 529-531 (1941)

⁷⁴ S. G. Mason, *Pulp Paper Mag. Canada* 48, No. 10: 76-80 (Sept., 1947)

⁷⁵ J. d'A. Clark, *Tech. Assoc. Papers* 25: 568-575 (June, 1942)

⁷⁶ W. B. Campbell, *Tappi* 32, No. 6: 265-271 (June, 1949)

⁷⁷ J. C. Brown, *Tappi* 38, No. 3: 130-137 (March, 1950)

⁷⁸ A. A. Robertson and S. G. Mason, *Pulp Paper Mag. Canada* 50, No. 13: 103-110 (Dec., 1949)

⁷⁹ L. Nordman, *Svensk Papperstidn.* 52, No. 18: 441-447 (Sept. 30, 1949)

TABLE V

EFFECT OF BEATING ON SPECIFIC SURFACE AND EFFECTIVE SPECIFIC VOLUME OF SULFITE AND KRAFT PULPS

Type of pulp	Beating time, min.	Freeness (Canadian standard), cc.	Effective specific volume, cc./g.	Specific surface, cm. ² /g.
Sulfite	0	669	4.40	10,200
Sulfite	7	559	4.90	14,700
Sulfite	11	498	4.86	19,100
Sulfite	15	416	5.25	23,400
Sulfite	18	320	5.12	32,000
Sulfite	21	242	5.15	38,500
Kraft	0	738	3.66	9,500
Kraft	10	703	4.57	9,700
Kraft	41	541	4.70	31,600
Kraft	54	429	4.87	41,600
Kraft	66	292	4.67	58,400

TABLE VI

EFFECT OF BEATING TIME ON SPECIFIC EXTERNAL SURFACE OF A STRONG AND BLEACHED SULFITE PULP BEATEN IN VALLEY BEATER

Beating time, min.	Specific External Surface	
	Strong sulfite, cm. ² /g.	Bleached sulfite, cm. ² /g.
0	12,000	13,000
20	26,000	14,000
40	30,000	17,000
60	34,000	18,000
80	42,000	20,000
100	..	25,000
120	..	29,000

Effect of Beating on Adsorption Capacity

Because beating has a relatively small effect on the internal surface, it has little or no effect on the sorption of dissolved substances of small molecular size and, in general, no important changes in sorption can be attributed to beating. Most investigators have found that beating has a negligible effect on the hygroscopicity of the pulp.⁸⁰ As mentioned previously, Seborg, Simmonds, and Baird⁸¹ obtained a 6% increase in hygroscopicity on extreme beating, but this is only a relatively slight increase which can be attributed to making a small area of new surface accessible to water molecules.

⁸⁰ O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 219-228 (Nov. 12, 1931)

⁸¹ C. O. Seborg, F. A. Simmonds and P. K. Baird, *Paper Trade J.* 107, No. 19: 223-228 (Nov. 10, 1938)

The adsorption of dyestuffs is not appreciably affected by beating,⁸⁰ although there is a slight increase in the adsorption of direct dyes.⁸² This can be explained on the basis that basic and acid dyes have small molecules which easily penetrate the fine pores of the cellulose fiber, regardless of whether the fibers have been beaten or not, whereas direct dyes are larger in size and their penetration is affected by any loosening of the fiber. It has been shown that beating causes the preferential adsorption of certain basic dyes, and this fact has been used in the development of a two-color differential stain containing a direct blue dye and a direct orange dye.⁸³ When this stain is properly applied, unbeaten fibers stain almost pure blue, whereas in beaten stocks, the fibrils, fiber debris, and bruised spots on the fibers stain orange.

There is other evidence of increased reactivity of the fiber attributable to beating. Strachan⁸⁴ found that the adsorption of positively charged ions was increased with increased beating, following the curve of typical adsorption isotherms. Meller⁸⁵ found in his work on alkaline purification of pulps that beating favored a better penetration of alkali to the interior of the fibers, which he attributed to an increase in the "surface" of the fibers. Rowland⁸⁶ reports that beating increases the affinity of pulp for hydrous alumina to an appreciable extent, and Kress and Bialkowsky⁸⁷ also found that beaten pulp adsorbs twice as much alumina (from alum) as unbeaten pulp, although the total amount was small in both cases (0.15 and 0.30% on the air dry pulp). In the case of the adsorption of ions, the results are difficult to explain, but in the case of alumina, the effect is probably due to the relatively large size of the alumina floc which prevents its penetration into the smaller pores of the fiber until they are opened up by beating.

Minor Effects of Beating

In addition to the major effects discussed in the above sections, beating brings about certain minor changes in the fiber. For example, beating may squeeze out resins and impurities from within the fibers, and although this is not important on most pulps, it may be important on overcooked pulps where the ray cells, which contain most of the resin, are extremely fragile. Another effect which has been noticed on certain pulps (notably sulfate pulps) is a progressive increase in the pH value as the stock is

⁸² J. Strachan, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 13, Part 1: 61-81; 14, Part 2: 447-451 (Oct., 1932; March, 1934)

⁸³ F. L. Simons, *Tappi* 33, No. 7: 312-314 (July, 1950)

⁸⁴ J. Strachan, *Paper-Maker* 110, No. 5: TS 37-38 (Nov., 1945)

⁸⁵ A. Meller, *Paper Trade J.* 125, No. 11: 125-128 (Sept. 11, 1947)

⁸⁶ B. W. Rowland, *Paper Trade J.* 111, No. 9: 101-104 (Aug. 29, 1940)

⁸⁷ O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 219-228 (Nov. 12, 1931)

beaten. This increase in alkalinity is undoubtedly due to alkali left in the pulp fibers through improper washing in the pulp mill. Hall and Woodson⁸⁸ concluded that squeezing of the fibers by the action of the beater roll bars tends to bring this residual alkali to the surface of the fibers. Kanamaru⁸⁹ found by streaming potential measurements that the electrokinetic potential of sulfite fibers increased from -12 to -18 millivolts on beating for sixteen hours.

Treatment of Pulp in Special Gyratory Machine (Curlator)

An interesting development in the field of fiber-treating equipment has been the Curlator.* This machine has a unique action on pulp fibers and produces results entirely different from those obtained with other fiber-treating equipment. The development is very recent and, so far, has not been thoroughly tried, but preliminary results have been reported.

In the Curlator, the stock for treatment is supplied from a headbox to the center of the machine from which it progresses radially outward while being treated between a stationary plate and a gyrating upper plate. The treated stock is picked up by a rotating turntable at the periphery of the treating zone and doctored off. The stock enters the Curlator at about 3 to 4% consistency, but is thickened by the action of the plate to a consistency of approximately 20%. The white water extracted during treatment is then reunited with the stock immediately after treatment.

During the treating process, the stock is formed into nodules, and these nodules are rolled in different directions under compression so that there is no slip between fibers. Pressure is maintained on the nodules of the order of 1800 p.s.f. of plate area, although operating pressures are usually under 15 p.s.i. on the surface contacting the pulp. The gyratory surface speed of the upper plate is below 300 f.p.m.⁹⁰ The clearance between working surfaces and the temperature of the stock can be adjusted to obtain the desired results.

The Curlator treats the fiber in such a way that it produces a permanent change in the shape of the individual fibers toward more bends, kinks, and twists in the fiber. The effect obtained in the Curlator is somewhat the same as can be obtained by rolling a nodule of high-consistency pulp with a circular motion between the thumb and finger, or by rolling a handful of pulp at about 20% consistency on a piece of coarse canvas, using the flat of the hand and a gyratory motion.⁹¹

* Curlator Corp., 565 Blossom Road, Rochester, N. Y.

⁸⁸ G. Hall and W. S. Woodson, *Paper Trade J.* 88, No. 4: 51-55 (Jan. 24, 1929)

⁸⁹ K. Kanamaru, *J. Soc. Chem. Ind. (Japan)* 34, 34B (1931)

⁹⁰ F. P. Silver, *Paper Trade J.* 128, No. 9: 75-80 (Mar. 3, 1949)

⁹¹ H. S. Hill, J. Edwards and L. R. Beath, *Paper Trade J.* 128, No. 11: 92-100 (Mar., 17, 1949)

Treatment in the Curlator generally results in an increase in freeness, decrease in burst and tensile, decrease in stiffness, increase in tear, increase in stretch, and increase in bulk (after shives are removed). The effects of the Curlator are quite different from those obtained on beating, and in many cases are directly the opposite. The paper formed from the treated pulp is softer, more opaque, and more porous than paper made from untreated pulp. The loss in tensile and bursting strengths and the increase in tearing strength obtained on "Curlated" pulp are probably due to the lower degree of fiber contact resulting from the increased number of bends, kinks, and twists in the fibers. The increase in porosity can be explained partly in this way, and partly on the basis that the fibers are given a more tubular cross section. The typical matte and opaque appearance of papers made from the treated fibers is caused by the increase in fiber contortion, which results in more scattering of light.

The results obtained depend upon the type of pulp used. Unbeaten pulps, for example, do not show the same decrease in burst and tensile strengths and increase in tearing strength as do beaten pulps for the reason that they are near the extremes of these values anyway. Groundwood is more resistant to treatment than the chemical pulps. In addition to its above purpose, the Curlator can also be operated as a refiner.

Factors Affecting Beating

Many factors affect the rate and type of beating. One of the most important is the type of beating or refining engine and the way in which the equipment is operated. For example, in the case of the beater, slowly beaten pulp generally has a higher strength than pulp which has been beaten rapidly, and other factors of importance are the condition of roll and bedplate bars, consistency of the stock, amount of pressure exerted by the roll, etc. These factors have already been discussed, and some of the more important pulp and stock properties will be discussed in the following sections for their effect on the beating operation.

Beating Different Pulps

The beating qualities of the various commercial pulps differ considerably. The practical papermaker recognizes this fact, and in mixed furnishes he sometimes makes a practice of adding and partially beating the harder-beating pulp before the other pulp is added to the beater. For example, in mixed furnishes of rag and sulfite pulp, the rag is furnished to the beater first and usually is beaten for several hours before the sulfite pulp is added. In a four-hour beating cycle, the sulfite would usually be added two hours after the rag pulp, and in an eight-hour beating cycle, such as might be used for ledger paper, the sulfite pulp would be added about five

to six hours after the rag pulp. This difference in beating qualities is generally recognized when using mixtures of sulfite-rag, sulfite-soda, or sulfite-kraft, but there are also differences in the beating qualities of bleached and unbleached pulps of the same grade which greatly affect the results obtained.⁹² The most desirable method for handling mixed furnishes would be to beat each pulp separately and blend the fully beaten pulps in a chest, but most paper mills do not have the space nor the equipment to handle stock in this manner.

The optimum time of beating differs, depending upon the type of fiber and the grade of paper in which it is to be used. Wood pulps vary considerably in their beating properties, even when cooked by the same process. Hardwood pulps, as a rule, must be beaten to much lower freeness values than softwood pulps to obtain anywhere near equivalent strength values.⁹³ Western hemlock sulfite is generally much harder to beat than spruce sulfite. Very few pulps are prepared with an eye toward maximum wetting ability, as this requires long cooking times at low temperatures, which is costly and, in addition, not all papers require this property in the pulp. However, pulps which are to be used for the production of strong, non-porous papers such as bonds and charts must have good "wetting" properties, and pulps for certain grades such as glassine and greaseproof require the maximum in wetting ability.

Some non-woody pulps require exceptionally long beating periods. For example, linen fibers for cigarette papers are customarily beaten from 15 to 30 hours in a conventional Hollander beater. Manila rope stock is generally beaten from eight to twelve hours, and rag or manila stock used in the manufacture of carbon tissues often requires from twenty to thirty hours of beating. On the other hand, straw pulps are exceptionally easy to beat and have been used (although not in the United States) in lightweight cigarette, Bible, and similar papers to give "rattle." For example, wheat straw pulps and bagasse develop maximum strength after only twenty to thirty minutes beating, compared with a time of forty to sixty minutes required for wood pulps under the same beating conditions.⁹⁴

Drying of pulp brings about a change in the beating properties, since once pulp has been dried, loosening of the fibers becomes more difficult, perhaps because of a drying of some residual hemicellulosic material, or simply a contraction of the cellulose structure. The self-contained mill in most cases receives pulp in slush form in consistencies of 3 to 15% so that

⁹² O. Kress and F. W. Brainerd, *Paper Trade J.* 98, No. 13: 163-167 (Mar. 29, 1934)

⁹³ G. Haywood, *Tappi* 33, No. 8: 370-383 (Aug., 1950)

⁹⁴ S. I. Aronovsky, A. Rhodes and E. C. Lathrop, *Paper Trade J.* 124, No. 13: 49-54 (Mar. 27, 1947)

drying is not a problem, but paper mills which are not located near a pulp mill must obtain their pulp in roll, lap, or dry baled sheets. Improper drying of this pulp has been known to affect adversely the strength of the fiber.⁹⁵ As a rule, dried pulp does not beat so easily, nor does it produce paper with as high a bursting strength as slush pulp. Cameron^{95a} found that oven-dried pulps were about 10 to 15% weaker than air-dried pulps. The results of Lyne and Galley^{95b} showed a linear relationship to exist in the case of unbeaten pulps between the per cent loss in bursting strength of the pulp and the dryness of the pulp, so that only 15% of the original strength remained when the pulp was reduced to the oven-dried state. The loss obtained was much less in the case of beaten pulps and was less with sulfate than with sulfite pulps.

Drying tends to increase opacity; e.g., Parsons⁹⁶ obtained an increase in opacity from 77.3 to 81.0 when dry-lap pulp was substituted for wet-lap pulp (bleached poplar sulfite). This increase in opacity is of value for certain printing papers, but mills making glassine papers must use wet-lap, slush pulp, or 75 to 85% air-dry pulp rather than fully dried pulp. Bleaching affects the beating properties, since overbleached pulps tend to go to pieces much more quickly than unbleached or slightly bleached pulps.

Kress and Bialkowsky⁹⁷ showed that when well "hydrated" stock is formed into sheets, air-dried, and then disintegrated and soaked in water for a long period of time, it reverts to its original soft and "greasy" feel and forms a strong sheet of paper, thereby indicating that swelling of pulp fibers is reversible. The reswelling process is extremely slow in some cases, but if time is allowed, most beaten and dried pulps will revert to a "hydrated" state on soaking. The swelling process is not always completely reversible, particularly if the product has been dried at high temperature. This is an important consideration in the repulping of dry broke, and it is a fact well known by paper chemists that wet and dry broke behave differently in the beater. One difference is that dry broke tends to be weaker than the original pulp.

The proportion of springwood and summerwood fibers in a pulp has an affect on the beating properties. All pulps differ somewhat in the proportion of these fibers, and some pulps (notably the pines) are characterized by a greater difference between the summerwood and springwood fibers than is usually the case. In general, springwood fibers are thinner walled and more flexible than summerwood fibers and, as a result, tend to collapse

⁹⁵ S. E. Ekman, *Paper Trade J.* 123, No. 8: 88-92 (Aug. 22, 1946)

^{95a} E. P. Cameron, *Pulp Paper Mag. Canada* 22: 448-450 (Apr. 24, 1924)

^{95b} L. M. Lyne and W. Gallay, *Tappi* 33, No. 9: 429-435 (Sept., 1950)

⁹⁶ S. R. Parsons, *Paper Trade J.* 115, No. 25: 314-322 (Dec. 17, 1942)

⁹⁷ O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 219-228 (Nov. 12, 1931)

into a ribbon-like structure on beating, whereas the stiff thick-walled summerwood fibers remain in tubular form.⁹⁸ The effect which springwood and summerwood fibers have on the properties of the paper is discussed in the next chapter.

Effect of Hemicellulosic Material on Beating

It is now generally recognized that the presence of the less resistant forms of cellulose, i.e., the beta and gamma celluloses, cellulosans, and polyuronides, has an important influence on the beating qualities of pulp. Schwalbe⁹⁹ recognized as early as 1927 that these hemicellulosic substances were desirable in pulp for the production of strong papers and since that time, many other investigators have shown that there must be a minimum amount of these materials present.

Pulps which are low in hemicelluloses are very resistant to beating and have poor strength characteristics, whereas pulps which contain a high percentage of hemicelluloses beat very quickly and produce strong sheets. If a wood pulp is purified by alkali extraction to the point where it contains about 99% alpha cellulose, it cannot be beaten at all and will not make satisfactory paper, inasmuch as the fibers do not swell in water and remain in a shrunken condition.¹⁰⁰ Cottrall¹⁰¹ has shown that pulps high in alpha cellulose tend to be more fragile on beating than pulps high in gamma cellulose. If the amount of degraded cellulose in a pulp is increased through bleaching or by acid degradation, the pulp will tend to beat more readily and may even, in some cases, produce stronger paper than the untreated pulp if the degradation has not been carried too far. Holocellulose is known^{102, 103} to beat in a remarkably short time and even to reach the glassine stage in less than thirty minutes. The development of bursting strength is extremely rapid with holocellulose, due to its rapid "wetting" properties, and very little beating is required to reach maximum strength, after which further beating weakens the fibers.

During the period from 1931 to the present, much work was carried out on the effect of hemicelluloses on the beating qualities and strength of wood pulps. In many cases the evidence points to a direct relation between the hemicellulose content and the "hydrating" qualities of wood pulp.

⁹⁸ C. E. Curran, *Paper Trade J.* 103, No. 11: 200-204 (Sept. 10, 1936)

⁹⁹ C. G. Schwalbe, *Papier-Fabr.* 25: 481-485 (1927)

¹⁰⁰ F. E. Brauns and H. F. Lewis, *Paper Trade J.* 105, No. 10: 35-37 (Sept., 1937)

¹⁰¹ L. G. Cottrall, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 25: 175-181, Discussion 182-198 (Dec., 1944)

¹⁰² G. J. Hajny and G. J. Ritter, *Paper Trade J.* 111, No. 22: 281-282 (Nov. 28, 1940)

¹⁰³ H. H. Houtz and E. F. Kurth, *Paper Trade J.* 109, No. 24: 326-329 (Dec. 14, 1939)

Young and Rowland¹⁰⁴ showed in the case of softwood pulps that an alpha pulp (which contained less than 2.5% pentosans) had a swelling or "hydration" capacity of only about 4%, compared with a 96% swelling capacity for a southern kraft pulp (12.6% pentosans). Thus, the most likely explanation for the role which hemicelluloses play in the beating of pulp lies in the highly hydrophilic nature of this material. This hydrophilic nature of the hemicelluloses, which is accounted for by the relatively short chain length of this material, causes the fibers to absorb a great quantity of water and to develop into a gelatinous "hydrate,"¹⁰³ thus producing swelling and pushing the fibrillae apart to produce fibrillation. The highly "gelatinous" surface produced by this material is responsible for the strong bonds formed when the fibers are dried in the final sheet.

Many other examples, aside from those given above, can be cited to substantiate the general rule that the greater the amount of hemicellulosic material in the pulp, the faster the beating. In general, it may be stated that wood pulps which are well cooked but not overdegraded will contain a high percentage of hemicellulosic material and will be characterized by rapid beating qualities and good strength qualities. Thus, slow-cooked sulfite or Mitscherlich pulp contains a higher proportion of hemicellulosic material and consequently "wets up" more quickly in the beater than a drastically cooked sulfite. Sulfite pulp made from the western woods of the United States, which are relatively low in hemicellulose, develop "slowness" rather slowly on beating. Hardwood pulps wet more rapidly than spruce when both are cooked by the sulfite process because of the higher pentosan content of hardwoods. Fries¹⁰⁵ was able to make an easy-beating pulp from poplar by cooking by the semichemical process under conditions such that the pulp contained a very high percentage of undegraded hemicellulose.

The impression should not be given that there is always a direct relationship between pentosan or hemicellulosic content and the beating qualities of pulp. On the contrary, it is well known that bleached hardwood soda pulp, which is normally high in pentosan content, is a slow-beating pulp. Referring again to the work of Young and Rowland,¹⁰⁴ it can be seen that the correlation between pentosan content and swelling properties is far less satisfactory for hardwood pulps than it is for softwood pulps. This appears to be due to a difference in the manner by which the pentosans are held in the two pulps. Recent work¹⁰⁶ has shown that the amount of alkali extractable hemicellulose is a more reliable indication of

¹⁰⁴ G. H. Young and B. W. Rowland, *Paper Trade J.* 97, No. 15: 44-46 (Oct. 12, 1933)

¹⁰⁵ K. W. Fries, *Paper Trade J.* 112, No. 21: 223-224 (May 23, 1946)

¹⁰⁶ R. E. March through L. E. Wise, *Paper Ind.* 29, No. 6: 825-829 (Sept., 1947)

the beating qualities than the total hemicellulosic content. Apparently the pentosans which are closely linked with the cellulose have little effect on the hydrating properties, and it is the pentosans associated with the hemicellulose fraction which are important in determining beating qualities. Hägglund and Webjorn¹⁰⁷ point out that it is the low polymerized polyoses which are responsible for easy beating, and that the highly polymerized forms do not increase the swelling or make the pulp easy beating. Cottrall^{107a} has shown that paper made from sulfite pulp from which the alkali-soluble hemicelluloses have been removed has a lower bursting strength, lower tearing resistance, and higher opacity compared to paper made from unextracted pulp. The lower tearing resistance indicates that the fibers are so embrittled by removing the alkali-soluble hemicelluloses that they fragmentize, rather than fibrillate, under the action of the beater roll. The lower bursting strength and higher opacity suggest that fiber bonding is not fully developed in the pulp from which the alkali-soluble hemicelluloses have been removed.

Cotton or rag pulps are an exception to the above statements, since they form strong papers in spite of their low content of hemicellulose (usually less than 1%). The explanation seems to lie in the fact that cotton or rag pulps fibrillate to a greater extent than wood pulps and unravel into long, very fine fibrils which become entangled to form a strong sheet. However, because of their low hemicellulosic content, cotton pulps are much more difficult to beat than wood pulps and require a much longer time in the beater. Moreover, Obermanns¹⁰⁸ showed that the addition of hemicellulosic material, namely, xylan and beta cellulose, increases the rate of "hydration" and strength characteristics of rag pulp. In the same connection, Musser and Engel¹⁰⁹ found that cotton pulps with the lowest viscosity undergo the most rapid beating and that chemical degradation of cotton pulp increases the rate of beating. The results of Crain¹¹⁰ reproduced in Figure VI-3 show that the time of beating required to reach a freeness of 400 cc. decreases appreciably as the viscosity of rag stock is lowered by bleaching. Thus, decreasing the viscosity of rag pulp reduces the resistance of the fiber to the mechanical action of the beater. However, the viscosity must be reduced to a considerable extent before the mechanical action is enhanced, and it has been noted that about the point where the

¹⁰⁷ E. Hägglund and B. Webjorn, *Svensk Papperstidn.* 52, No. 6: 131-137 (March 31, 1949)

^{107a} L. G. Cottrall, *Tappi* 33, No. 9: 471-480 (Sept., 1950)

¹⁰⁸ H. E. Obermanns, *Paper Trade J.* 103, No. 7: 109-117 (Aug. 13, 1936)

¹⁰⁹ D. M. Musser and H. C. Engel, *Paper Trade J.* 113, No. 2: 13-16 (July 10, 1941)

¹¹⁰ R. C. Crain, *Paper Trade J.* 103, No. 24: 343-352 (Dec. 10, 1936)

beating rate is appreciably increased, a significant decline in the quality of the paper occurs (see Chap. VII).

Effect of Lignin on Beating

Another important factor in determining the beating qualities is the lignin content of the pulp. Once the lignin has been removed from wood by cooking, it is relatively easy to loosen the individual fibers by slight mechanical action. In fact, Ritter has pointed out that wood from which the lignin and hemicelluloses have been removed can be easily dissected into fibrils, provided it has not been allowed to dry out.

Hall¹¹¹ concluded in the case of sulfate pulps that the ease of beating is inversely proportional to the lignin content and that sulfate pulps con-

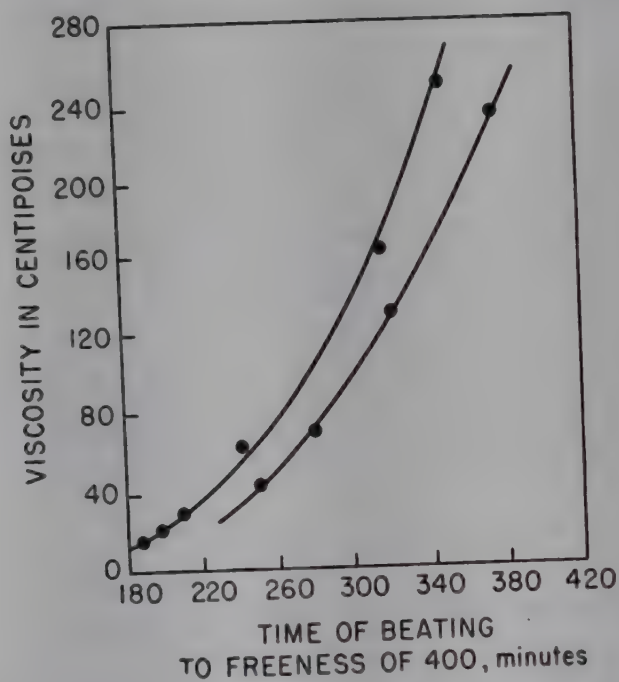


Fig. VI-3. Effect of viscosity of rag (muslin) stocks on rate of beating.

taining a high percentage of lignin are likely to have a high freeness and a low strength and have slow beating properties. This agrees with the results of Lewis and Richardson¹¹² shown in Figure VII-2. The relationship between rate of beating and lignin content is not so clear-cut with sulfite pulps, since raw sulfite pulps contain a high content of hemicellulosic material, in addition to a high lignin content, and the rapid hydrating qualities of this material tends to offset the effect of the lignin. However, Hägglund and Webjorn¹¹³ have shown that even with sulfite pulps,

¹¹¹ G. A. Hall, *World's Paper Trade Rev.* 96, No. 16: 1340, 1354, 1396 (Apr. 19, 1929)

¹¹² H. F. Lewis and C. A. Richardson, *Paper Trade J.* 109, No. 14: 188-190 (Oct. 5, 1939)

¹¹³ E. Hägglund and B. Webjorn, *Svensk Papperstidn.* 52, No. 6: 131-137 (March 31, 1949)

high lignin content makes the pulp difficult to beat in spite of the high percentage of easy-beating low-polymerized hemicellulloses which the pulp contains. Apparently the lignin protects these polyoses and prevents the taking up of water, since once the lignin is removed by chlorite treatment, the pulp becomes very easy to beat. Hall¹¹¹ concluded from his work that the differences in beating qualities and strength properties between direct cooked and indirect cooked sulfite pulps are greater than would be expected from the difference in their lignin contents.

In many cases there is a very positive relationship between the bleachability of a pulp and its beating qualities (see Ch. V). For example, Mason and coworkers¹¹⁴ found a direct relationship of almost linear value between bleachability and the rate of hydration of sulfite pulp in the British Standard Disintegrator.

Effect of Temperature on Beating

Temperature is an important variable in the beating of pulp, and in many paper mills there is sufficient difference in water temperature between the winter and summer months to affect the beating qualities. In the winter, the temperature may drop as low as 5° C., whereas in summer it is a common occurrence in the beating of rag or glassine pulps, which require long beating, to have the temperature of the stock rise to a high of 70° C. The extent of temperature rise on beating varies with the type of stock and the time of beating, as shown in Table VII.¹¹⁵

TABLE VII
EFFECT OF TIME OF BEATING ON TEMPERATURE

Type of paper	Beating time	Temperature rise, 0° F.
Fine tissue from rags	8 hr.	51°
Esparto	3 hr.	23°
Kraft	2 hr. 30 min.	20°
Kraft	2 hr. 10 min.	17°
Sulfite wrapping	1 hr. 40 min.	13°

Lewis and Gilbertson¹¹⁶ found that the fastest beating in the case of rag stock takes place at a temperature of 25° C., being faster at this temperature than at 6 or 45° C. Stephenson¹¹⁷ studied beating of bleached sulfite

¹¹⁴ N. S. Grant, O. A. Mason and H. F. Donnelly, *Pulp Paper Mag. Canada* 48, No. 3: 151-158, Convention Issue (1947)
¹¹⁵ Patented Beater. "A Study of the Beater." Bertram's Ltd., St. Katherines Works, Sciennes, Edinburg 9. (Feb., 1927, Feb., 1936)
¹¹⁶ H. F. Lewis and L. A. Gilbertson, *Paper Trade J.* 100, No. 15: 189-195 (Apr. 11, 1935)
¹¹⁷ J. N. Stephenson, *Paper* 17, No. 26: 16-19, 34 (March 8, 1916)

at 23, 50, and 64° C. and concluded that lowering the temperature of beating increases the burst, breaking length, folding endurance, and stretch, using a constant time of beating of five hours. Hall¹¹⁸ found that beating was accelerated as the temperature of beating was lowered from 30 to 6° C. in the case of kraft pulp beaten in a Lampen mill. On the other hand, Clark¹¹⁹ found that, using a laboratory kollergang, temperature had little effect on beating in the temperature range of 25 and 40° C.

Hall's work¹¹⁸ on kraft pulp indicated that the increase in strength noted at lower temperatures is due to increased beating rate, since when the pulp was beaten to the same freeness, the final strengths were the same in every case. However, Lewis and Gilbertson¹²⁰ found that the strength of rag papers was higher at the lower temperatures, even when the stock was beaten to the same freeness. Renaud¹²¹ obtained the maximum strength at about 30° C. in the case of cotton pulps. The temperature at which the paper is formed is a factor and, in this connection, Rubin¹²² noted that the strongest paper was made in his mill in the fall and spring, when the water temperature at the machine was about 5 to 10° C., and Hatch¹²³ noted that the strongest paper was made in the winter time.

In a recent study on the beating of strong sulfite pulp in a Noble and Wood laboratory beater, Libby and Ronning¹²⁴ found that beating rate was increased progressively when the temperature of beating was lowered from 80 to 5° C. when wet-lap pulp was used. On the other hand, when dry-lap pulp was used, the fastest beating occurred at an intermediate temperature of 30° C., and beating rate was very slow at low temperatures. The slow beating of dry-lap pulp at low temperatures is probably due to the slow removal of air from the relatively dry fibers at the low temperature.¹²⁵ The strength of sheets made from the beaten pulps at the same drainage time did not coincide with the rate of beating curves, since higher strengths were obtained at the higher beating temperatures, with 40° C. giving the best all-round strength results. This higher strength at higher temperatures is contrary to the results of most other investigators, and apparently the difference in results depends to a large extent upon the type of beat-

¹¹⁸ G. Hall, *Tech. Sec. Proc., Paper Makers' Assoc. Gt. Britain Ireland* 18, Part 1: B229 (Oct., 1937)

¹¹⁹ J. d'A. Clark, *Tech. Assoc. Papers* 18, No. 1: 158-166 (June, 1935)

¹²⁰ H. F. Lewis and L. A. Gilbertson, *Paper Trade J.* 100, No. 15: 189-195 (Apr. 11, 1935)

¹²¹ R. Renaud, *Paper-Maker* 109, No. 2: 103-117 (Feb., 1950), translated from the French

¹²² M. M. Rubin, *Paper Trade J.* 101, No. 6: 67-71 (Aug. 8, 1935)

¹²³ R. S. Hatch, *Paper* 19, No. 20: 18-19 (Jan. 24, 1917)

¹²⁴ C. E. Libby and O. K. Ronning, unpublished Thesis, "The Influence of Temperature during the Beating Process," New York State College of Forestry, Syracuse, N. Y. (Feb., 1949)

ing, i.e., whether the beater is set up so that "wet" beating or "cutting" is the predominating action. Libby and Ronning¹²⁴ found that lower beating temperatures result in a higher drainage time, even at the same freeness value.

If a long, slow stock is desired, the temperature of the stock should be kept low during the beating period, and for best results, well water should be used, since this generally has a low temperature even during the summer months. Water from shallow ponds or water previously used for cooling is usually too high in temperature. Warm water is particularly unsuited for the beating of rag and manila rope stock used in the manufacture of manifold, bonds, twisting, and similar grades of paper where long beating periods are required. In general, the type of beating which produces the desired results with the smallest temperature rise is the most efficient.

The favorable effect which low temperature has on pulp fibers can be partly explained by the fact that fiber swelling is an exothermic reaction, and hence the extent of swelling is increased the lower the temperature.¹²⁶ Cellulose, like its ethers, is probably more nearly "soluble" in cold water than in hot water, and thus a low temperature is more favorable for beating and fiber bonding. If cellulose fibers are heated to high temperatures, they apparently become more or less dehydrated, which causes them to shrink and become brittle. Lewis and Gilbertson¹²⁷ examined rag stock which had been beaten in both cold and hot water and noticed that the fibers beaten at high temperature were much more brittle and the fibrillation was coarser and there was less of it than with the fibers beaten at low temperature. Renaud¹²⁸ noted that cotton fibers decrease in diameter from 30 to 20 microns upon heating from 18 to 60° C., the swelling process being reversible up to about 70 to 80° C. Wood pulps are not so sensitive to temperature as rag pulps, but it is well known that stock which is too highly "hydrated" for good machine operation can be made "free" by heating with steam. Heating to the boiling point results in a permanent change in beaten fibers,¹²⁹ unless the fibers are again beaten.

¹²⁵ J. Strachan, *Tech. Sec. Proc., Paper Makers' Assoc. Gt. Britain Ireland* 6: (March, 1926)

¹²⁶ E. Tolvi, *Paper and Timber (Finland)* 32, No. 3 (March, 1950)

¹²⁷ H. F. Lewis and L. A. Gilbertson, *Paper Trade J.* 100, No. 15, 189-195 (Apr. 11, 1935)

¹²⁸ R. Renaud, *Paper-Maker* 109, No. 2: 103-117 (Feb., 1950), translated from the French

¹²⁹ J. d'A. Clark, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 24: 30-54 (Dec., 1943)

Effect of Added Substances

Pulp is never beaten in pure water, since the process water contains natural impurities and other added substances, such as alum, rosin size, starch, sodium silicate, dyestuffs, and pigments. These latter substances are usually added for some specific purpose, their effect on the beating being incidental, but in some cases, chemicals may be added to the beater to "soften" the pulp. For example, sodium silicate is sometimes added to increase the rate of beating.

The presence of hemicelluloses has a very pronounced effect on the beating of cellulose fibers, as has already been explained, and other hydrophilic colloids are also important. Bell¹³⁰ has stated that glucose has an accelerating effect on beating and may be employed to promote the beating of stock for glassine. Methylcellulose appears to have a marked

TABLE VIII

EFFECT OF ADDED CHEMICALS ON THE STRENGTH OF SULFITE PULP
DEVELOPED BY BEATING

Solution used	Bursting strength
Water	51.8
1% Na ₂ CO ₃	77.4
5% Na ₂ CO ₃	68.6
5% NaOH	72.2
5% ZnCl ₂	70.4
5% ammonia	73.6
5% H ₂ SO ₄	51.4
10% NaCl	52.0

accelerating effect on the beating rate of rag and chemical wood pulps. Formaldehyde also has a marked accelerating effect on beating, probably because of its swelling action on pulp fibers.¹³¹ On the other hand, gelatin appears to inhibit hydration,¹³¹ and rosin also is believed to have a retarding effect.

Strong solutions of acids, alkalies, and salts cause a marked increase in the amount of "hydration" on beating. For example, Mansfield and Stephenson¹³² obtained, in most cases, a marked increase in the bursting strength of bleached sulfite pulp on beating in a pebble mill in the presence of various chemicals for a given period of time. The results obtained are shown in Table VIII. Sutermeister¹³³ obtained smaller increases using a

¹³⁰ J. H. B. Bell, *J. Soc. Chem. Ind.* 52: 109-139 (1933)

¹³¹ D. M. Musser and H. C. Engel, *Paper Trade J.* 115, No. 8: 85-87 (Aug. 20, 1942)

¹³² E. K. Mansfield and J. N. Stephenson, *Paper* 19, No. 8: 17-19 (Nov. 1, 1916)

¹³³ E. Sutermeister, *Paper* 23, No. 14: 11-13 (Dec. 11, 1918)

different sulfite pulp, and found that soda pulps were much less susceptible to "chemical hydration" than sulfite pulps.

Ions have an important effect on pulp fibers, since cellulose is a gel and responds in a general way to ions of the Hofmeister series.¹³⁴ Strachan^{135, 136} believes that the effect of hydrated ions is sufficient to modify the rate and degree of "hydration," and pointed out as early as 1926 that fibrillation is essentially electrostatic and ionic in nature. Certain ions may peptize the surface molecules on pulp fibers, thereby producing a colloidal solution which is reversible on drying and rewetting. On the other hand, Rowland¹³⁷ mentions the adverse effect which aluminum and even calcium and magnesium ions have on the "hydration" of cellulose. Edge¹³⁸ also found evidence that the effect of positively charged hydrated ions is to retard "hydration" and fibrillation of the fibers. This adverse effect of positively charged ions on beating seems to be verified by the fact that the presence of alum in the pulp greatly increases the power consumption in the jordan.¹³⁹ For this reason, it is standard practice in some kraft mills to add a large part of the alum after the jordans.

The *pH* is another important variable in beating, and maxima in both swelling curves and rate of beating are known to occur at different *pH* values. Morgan and Libby¹⁴⁰ found in the case of cotton pulp that the minimum strength on beating was obtained at a *pH* between 4.0 and 4.5, and at a *pH* of 10. The maximum strength on beating was obtained at a *pH* of 8.5 which is close to optimum value, i.e., *pH* 8.0, reported by Renaud.¹⁴¹ Morgan and Libby found that sulfite pulp behaved differently in that the strength decreased as the *pH* value was lowered. Hansen¹⁴² also found that the beating of wood pulps was retarded by low *pH* values and was speeded up in alkaline medium in accordance with the greater swelling of cellulose fibers in alkaline medium. Other investigators have noted a minimum in both the swelling and degree of beating at a *pH* around 7.0 to 7.5.

Rich¹⁴³ points out that the cuprammonium viscosity is decreased

¹³⁴ B. W. Rowland, *Paper Trade J.* 101, No. 13: 194-196 (Sept. 26, 1935)

¹³⁵ J. Strachan, *Paper-Maker* 110, No. 5: TS 37-38 (Nov., 1945)

¹³⁶ J. Strachan, *Paper-Maker* TS 41-42 (May, 1946)

¹³⁷ B. W. Rowland, *Paper Trade J.* 101, No. 13: 194-196 (Sept. 26, 1935)

¹³⁸ S. B. H. Edge, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 18, Part 1: 5-10 (Oct., 1932)

¹³⁹ W. F. Gillespie and J. J. Goss, *Paper Trade J.* 124, No. 19: 206-212 (May 8, 1947)

¹⁴⁰ H. W. Morgan and C. E. Libby, *Paper Trade J.* 85, No. 19: 183-187 (Sept. 10, 1927); 85, No. 20: 194-201 (Nov. 17, 1927)

¹⁴¹ R. Renaud, *Paper-Maker* 109, No. 2: 103-117 (Feb., 1950), translated from the French

¹⁴² A. B. Hansen, *Paper Mill* 52, No. 40: 3, 6, 8 (Oct. 5, 1929)

¹⁴³ E. D. Rich, *Paper Trade J.* 112, No. 6: 63-68 (Feb. 6, 1941)

when the pulp is beaten in the presence of chemical substances such as alum, fillers, and colors. He noted a drop in viscosity from 3 to 25% when the pulp was beaten in the presence of chemicals which produced a low pH .

Pulp Testing

The papermaker judges pulp quality on the basis of color, cleanliness, and pulp strength, the last referring to the sheet-forming qualities. The tests used for measuring color and cleanliness are described later. The tests used for measuring pulp strength are discussed below.

Testing in the Beater

Pulp cannot be tested for strength on the basis of chemical and physical tests alone, and hence direct testing in the beater must be used. In testing pulp, the pulp is beaten in a small laboratory pebble mill or beater under carefully controlled conditions for a definite period, during which time samples are withdrawn from the beater at intervals for making into handsheets.¹⁴⁴ Handsheets are made on a standard sheet machine, pressed, and dried under controlled conditions, and then the sheets are tested for basis weight, thickness, tensile strength, stretch, bursting strength, tearing resistance, and folding endurance after conditioning the sheets at 70° F. and 50% relative humidity.

Freeness tests are made on the pulp at the time samples are withdrawn for making into handsheets. The results of the physical tests on the handsheets are usually plotted against freeness of the pulp, although it is preferable to plot the physical tests, including freeness, against beating time. Pulps are rated for strength in one of two ways: (1) on the basis of the maximum strength developed during beating or (2) on the basis of the strength developed at a given freeness or a given beating time. If the latter method is used, it is desirable to secure a sample of stock from the paper mill as a guide to the freeness and strength required for the particular grade of pulp under test. This sample should be taken from the wet press, rather than from the headbox, to eliminate the effect of the fines.

The rate of beating of a given pulp can be measured by plotting the tensile strength of the test sheets made from that pulp against the logarithm of the time of beating. A semilogarithmic plot is of value, since density, bursting strength, and tearing resistance generally decrease linearly as a function of the logarithm of the beating time.^{144a} The shape of

¹⁴⁴ See TAPPI Standards

^{144a} L. V. Forman, *Tappi* 33, No. 9: 444-450 (Sept., 1950)

the curve is a measure of the rate of beating. Bachman¹⁴⁵ suggests that pulps be evaluated on the basis of a relationship called "omega B," which is obtained by plotting tensile strength of handsheets versus time of beating of the pulp and calculating "omega B" from the slope of the curve at a given point.

$$\text{omega B} = \frac{100(1 - \text{slope of curve at a given point})}{\text{slope of a line from the given point to the origin}}$$

Omega B is 100 at the point where the curve passes through the origin. The area of surface and the potential bonding area of the fibers generally vary directly with beating time.^{144a}

The properties desired in a particular pulp depend upon the grade of paper in which it is to be used. Pulp used for making paper bags must be capable of forming strong paper. On the other hand, pulp to be used in the manufacture of printing papers does not require high strength, but instead must produce papers of high ink receptivity and high opacity.

Fiber Length Analysis

Wood fibers vary in length, width, and cell wall thickness according to the species, position of fiber in the tree, and conditions under which the tree was grown. Fiber dimensions are important in papermaking because they influence the density, strength, flexibility, smoothness, sizing, and dyeing properties of the paper. Hence, the analysis of pulp for fiber length is an important test. Fiber length is, however, only one of the many individual properties making up pulp (sheet-forming) strength, as will be shown in the following chapter, and does not furnish a direct measure of sheet-forming qualities.

Short fibers are less desirable from a papermaking standpoint than long fibers.^{146, 147} This is particularly true in the case of the fiber "fines." The fines are principally ray cells and, as such, are quite different in composition from the wood fibers and tracheids. For example, the fines in bleached sulfite pulp contain approximately ten times as much resinous material and a much greater amount of ash than the whole pulp.¹⁴⁷ On the other hand, the fines in groundwood have a lower lignin content and a higher pentosan content than the larger fibers.¹⁴⁸ In general, the fines of all pulps have a higher percentage of degraded cellulose and hemicellulosic material than the longer fibers, and this is manifested in an increased alkali solubility, increased copper number, and decreased viscosity. Fines

¹⁴⁵ Albert Backman, *Finnish Paper and Timber J.* 28, No. 7A: 35 (1946)

¹⁴⁶ O. Kress and F. W. Brainerd, *Paper Trade J.* 98, No. 13: 163-168 (March 29, 1934)

¹⁴⁷ R. B. Brown, *Paper Trade J.* 95, No. 13: 145-147 (Sept. 29, 1932)

¹⁴⁸ C. V. Holmberg and E. C. Jahn, *Paper Trade J.* 111, No. 1: 1-4 (July 4, 1940)

form a desirable part of a groundwood furnish as shown in the next chapter, but they are very undesirable in chemical wood pulps if present in too high a percentage, since they reduce the color and strength of the pulp and tend to produce pitch trouble on the paper machine. Typical sulfite pulps may contain up to 15 to 20% of fines, the exact amount depending upon the method of chip preparation and the cooking, bleaching, and pulp washing operations.

As a general rule, pulpwood fibers tend to increase in width with increasing fiber length up to a certain point, beyond which width remains about constant with any further increase in length.^{149, 150} The amount of moisture has an appreciable effect on fiber dimensions, accounting for 1 to 2% of the length and nearly 10% of the width. Highly purified, i.e., delignified, fibers swell more than raw fibers, and as a result, have slightly larger dimensions. The approximate average length and diameter of some of the common woody and non-woody fibers are given in Table IX. These results were obtained at the College of Forestry, State University of New York, and are based upon the analysis of a large number of different samples. The average values are on a numerical basis and include the fiber elements only, not the ray cells or vessel elements.

Fiber length distribution is equally as important as average fiber length. A pulp containing many long and many short fibers has quite different properties from a pulp containing fibers all of which are of nearly equal length, even when the two pulps have the same average length. Typical results on fiber length distribution in jack pine pulp are given in Table X.¹⁵¹ Reporting as a weighted average by weight minimizes the shorter fibers and is the method coming into general use. If the average on a number basis is reported, there is the question of deciding upon the shortest length to be considered which, according to Clark,¹⁵² should be any fibrous element having a length over 0.10 mm. and a projected area of over 0.10×0.01 mm. Klemm¹⁵³ suggested the following classification of fibers according to length and width:

Long fibers	2-3 mm.
Medium fibers	1-2 mm.
Short fibers	0.1-1 mm.
Wide fibers	0.025-0.040 mm.
Medium fibers	0.010-0.025 mm.
Thin fibers	0.002-0.010 mm.

¹⁴⁹ J. Strachan, *World's Paper Trade Rev.* 83: 2110-2114 (June 26, 1925)

¹⁵⁰ J. H. Graff and R. W. Miller, *Paper Trade J.* 109, No. 6: 51-57 (Aug. 10, 1939)

¹⁵¹ J. H. Graff, *Pulp and Paper Microscopy*, p. 7. Institute of Paper Chemistry, Appleton, Wis. (1942)

¹⁵² J. d'A. Clark, *Paper Trade J.* 115, No. 26: 328-334 (Dec. 24, 1942)

¹⁵³ P. Klemm, *Wochbl. Papierfabr* 59, No. 23A: 88-95 (June 9, 1928)

TABLE IX
FIBER DIMENSIONS OF SOME PAPERMAKING FIBERS
Woody Fibers

	Average length, mm.
<i>Hardwoods</i>	
Aspen (<i>Populus tremuloides</i>)	1.1
Yellow poplar (<i>Liriodendron tulipifera</i>)	1.4
Beech (<i>Fagus grandifolia</i>)	1.1
Yellow birch (<i>Betula lutea</i>)	1.4
Paper birch (<i>Betula papyrifera</i>)	1.3
Maple (<i>Acer rubrum</i>)	0.85
Tupelo gum (<i>Nyssa aquatica</i>)	1.8
Black gum (<i>Nyssa sylvatica</i>)	1.7
<i>Softwoods</i>	
White spruce (<i>Picea glauca</i>)	3.7
Red spruce (<i>Picea rubra</i>)	3.4
Balsam fir (<i>Abies balsamea</i>)	3.5
Jack pine (<i>Pinus banksiana</i>)	2.9
Sugar pine (<i>Pinus lambertiana</i>)	5.4
Hemlock (<i>Tsuga canadensis</i>)	3.7
Western hemlock (<i>Tsuga heterophylla</i>)	3.1
Loblolly pine (<i>Pinus taeda</i>)	4.2
Western yellow pine (<i>Pinus ponderosa</i>)	3.6
Douglas fir (<i>Pseudotsuga taxifolia</i>)	3.5
Redwood (<i>Sequoia sempervirens</i>)	6.3

Non-Woody Fibers

	Average length, mm.	Diameter, microns
Esparto	1.5	9.0
Straw	1.5	13.3
Linen	25.0	16.0
Cotton (staple)	18.0	20.0
Bamboo	3.0	14.0
Jute	2.0	20.0
Ramie	140.0	50.0
Manila	7.0	18.0
Corn	1.5	18.0
Bagasse	1.7	20.0
Hemp (true)	20.0	22.0

Graff and Miller¹⁵⁴ also divide the common papermaking wood fibers into three classes: short, medium, and long, on the following basis:

¹⁵⁴ J. H. Graff and R. W. Miller, *Paper Trade J.* 109, No. 6: 51-57 (Aug. 10, 1939)

By weight

Long fibers	1.5 mm. and over
Medium fibers	0.5-1.5 mm.
Short fibers	Up to 0.5 mm.

By number

Long fibers	0.5 mm. and over
Medium fibers	0.1-0.5 mm.
Short fibers	Up to 0.1 mm.

Microscopic Method. One of the methods of measuring fiber length is by means of the microscope. In this method of testing, a dilute suspension of fibers is made and this is added to a microscope slide by drops. After the water is evaporated, the fibers are stained with an iodine-iodide stain and then straightened out under a dissecting microscope using dissecting needles. After the fibers are lined up in parallel fashion, the length

TABLE X

FIBER LENGTH DISTRIBUTION OF UNBLEACHED JACK PINE (KRAFT) PULP

Dimensions, mm.	Number of fibers	Percentage ^a frequency	Percentage by weight
0.01-0.1	143	55.6	8.9
0.1 -0.2	46	17.9	6.4
0.2 -0.3	14	5.4	3.2
0.3 -0.4	4	1.4	1.3
0.4 -0.5	8	3.1	3.2
0.5 -1.0	12	4.7	8.0
1.0 -1.5	5	1.9	5.8
1.5 -2.0	9	3.5	15.2
2.0 -2.5	5	1.9	10.9
2.5 -3.0	4	1.6	11.0
3.0 -3.5	2	0.8	6.7
3.5 -4.0	2	0.8	6.9
4.0 -4.5	3	1.2	12.5

^a The percentage frequency is obtained by dividing the number of fibers of given dimensions by the total number of fibers and multiplying by 100.

of each fiber is measured by use of a calibrated eyepiece. At least two hundred fibers should be counted and the average length determined. This gives the average length on a number basis, and factors must be used to convert to a weight basis. One disadvantage of the microscopic method of measuring fiber length is that the weight factors necessary for converting from length to weight are open to question.

Screen Classification. Another method of measuring fiber length is by means of screen classification. Fiber classification by screens is based

upon the mechanical segregation of the fibers into classes of definite fiber length and the determination of the weight of fibers in each class. There are two principal screen classifiers, the Bauer-McNett and the Clark.

The Bauer-McNett classifier consists of a series of tanks, each of which is equipped with a screen of progressively diminishing mesh. In each tank, there is an agitator and a mid-feather parallel to the screen surface which helps to maintain a high uniform velocity of stock across the screen surface to orient the fibers approximately parallel with the screen, and at the same time to keep the screen face clean.¹⁵⁵ The screen plates are interchangeable and are furnished in the following combinations:

Coarse set: 14, 28, 48, and 100 mesh

Medium set: 20, 35, 65, and 150 mesh

Fine set: 28, 48, 100, and 200 mesh

In making a fiber classification, a dilute suspension of stock is added to the water in the first tank and the test run for a definite period of time. At the

TABLE XI

RETENTION OF FIBER ON SCREENS IN BAUER-MCNETT CLASSIFIER

Freeness	Screen size	Unbleached sulfite	Unbleached kraft	Bleached soda
870	14	58.9	68.5	0.5
	28	80.1	83.5	32.5
	65	90.5	93.1	78.4
	100	92.8	96.5	85.6
250	14	26.1	37.4	0
	28	39.8	56.4	4.4
	65	59.2	74.2	32.9
	100	68.7	81.8	57.3

end of this time, the fiber segregated in each tank is collected on a filter, dried, and weighed. Typical results obtained with the Bauer-McNett are given in Table XI for three different pulps at two different degrees of beating.

The Clark classifier consists of a semicircular tub divided into compartments in which four open screen, 13 in. in diameter, are mounted on a common shaft. During testing, a 5-g. sample of pulp is added to the classifier and water is passed through the classifier in such a way that the fibers are presented regularly to the screen surface, through which they will pass if their length is less than twice that of the screen openings.¹⁵⁶ When

¹⁵⁵ W. T. Butler, *Pulp Paper Mag. Canada* 49, No. 3: 133-136 Convention Issue (1948)

¹⁵⁶ A. E. Reed and J. d'A. Clark, *Tappi* 33, No. 6: 294-298 (June, 1950)

classification is complete, the pulp held in each compartment is drained onto a 200-mesh wire screen attached to a box at the bottom of each compartment. The fiber pads obtained are then pressed, dried, and weighed.

Original data obtained with screen classifiers are in the form of percentage weight distribution between screens of different mesh. In making calculations of average fiber length from the amounts of the various screen fractions, it must be assumed that all the fibers have the same specific gravity and same diameter and that each unit weight has the same total fiber length, or it must be assumed that the percentage by weight of a fraction represents the relative total number of fibers in that fraction.^{157, 158} Results are converted to average length values by first establishing factors (using microscopic technique) showing the relationship between mesh size and weighted average fiber length. The average length of the fraction collected on the coarsest screen will vary according to the pulp used, and consequently separate factors must be determined for each pulp, but the factors for the intermediate fractions do not change appreciably for different pulps or for different degrees of beating.¹⁵⁹ Separate factors must be determined for each different classification condition used. The very fine fraction which passes through all screens and is lost in the effluent must be assigned an estimated value. For the Clark classifier, using a 5-g. sample, 12.5 liters of water per minute, and a classification time of four minutes, the following weighted average fiber lengths by weight were obtained for each compartment:¹⁵⁹

On 14-mesh	3.85 mm.
Between 14- to 28-mesh	2.70 mm.
Between 28- to 48-mesh	1.70 mm.
Between 48- to 100-mesh	0.95 mm.
Through 100-mesh	0.10 mm. (assumed)

Results on the basis of arithmetical average fiber length can be converted to a more useful value—weighted average fiber length by weight—by using approximate conversion factors established by Clark as +12½% for the Bauer-McNett classifier and +8% for the Clark Classifier.

Classification with Grid. A method of measuring approximate fiber length is by means of the de Montigny grid.^{160, 161} This method, like the

¹⁵⁷ E. R. Schafer and L. A. Carpenter, *Paper Trade J.* 90, No. 17: 57 (May 8, 1930)

¹⁵⁸ E. R. Schafer and M. Santaholma, *Paper Trade J.* 97, No. 19: 224-229 (Nov. 9, 1933)

¹⁵⁹ A. E. Reed and J. d'A. Clark, *Tappi* 33, No. 6: 294-298 (June, 1950)

¹⁶⁰ R. de Montigny and P. Zborowski, *Tech. Assoc. Papers* 29: 220-232 (June, 1946)

¹⁶¹ L. Schlick, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 14, Part II: 321-373 (March, 1939)

screen classification method, does not give a true measure of fiber length, but merely serves as an estimate or indirect indication of that property. The de Montigny grid consists of twenty-seven equally spaced, fixed vertical blades past which a dilute suspension of pulp stock is made to flow during the period of the test. The blades are set in a frame forming a grid which is placed in the standard British sheet machine replacing the regular grid plate. In carrying out the test, the sheet mold is filled with stock, drained, and the fibers retained on the blades of the de Montigny grid are collected. This is done three times, and the total amount of collected fiber is dried and weighed. One-third the weight in grams is then taken as the "fiber length index." The value of fiber length index obtained in this way is influenced by the amount of stock used in the test, as well as by other factors, but when carried out under constant conditions, the results appear to approximate a function of the average by weight of the square root of the fiber length. The relation between fiber length and fiber length index is different for different types of pulps.

Gelatinization by Chemical Means

When paper or pulp is treated with zinc chloride, sulfuric acid, etc., at high concentrations, the fibers undergo considerable swelling and then shrink on drying to form a dense, hard product. In some cases, these strong swelling agents enter the crystalline areas of the cellulose fiber and result in a rearrangement of the cellulose molecules. These processes are used commercially to produce vulcanized fiber and vegetable parchment.

Vegetable Parchment

In the manufacture of vegetable parchment, paper is passed through a bath of cold 55° Bé sulfuric acid, after which the sheet is neutralized with ammonia and finally washed thoroughly with water. The final product is a hard, dense sheet which is very useful as a greasproof wrapping. The product has considerable wet strength and is sometimes used when a high degree of permanent wet strength is required.

Vulcanized Fiber

Vulcanized fiber is a paper product which is used for electrical insulation, luggage, and as a building material for mechanical assemblies. This product is manufactured by passing a specially made paper through a 70° Bé bath of zinc chloride at 110° F. After the sheet has been passed through the bath, it may be combined with similarly treated sheets and then run between heavy squeeze rolls to unite as many as twenty plies of paper into a single unit. The swelling agent is then removed by washing the sheet in water, and finally the sheet is pressed, calendered, and dried. One

process of making vulcanized fiber involves the following steps:¹⁶² (1) gelatinization of the paper in a bath of zinc chloride, (2) winding of the paper on heated cylinders to produce several plies, (3) cutting the cylinder and then soaking in weaker and weaker solutions of zinc chloride, and finally in pure water, until all the chemical is removed, (4) finally drying and pressing into flat sheets.

Zinc chloride acts as a typical swelling agent, that is, it causes the fiber to increase in diameter and the fibrils to unwind. It is possible to precipitate the cellulose from its dispersed state by dilution with water or removal of the zinc chloride. Unlike the mechanical action of the beater, which only breaks the fiber into the relatively coarse fibrils, zinc chloride in high concentrations disperses the fibers to individual molecules or crystallites.

In practical operation, the rate of swelling is important and must be carefully controlled, because if the speed of gelatinization becomes too rapid, it closes the pores at the surface of the sheet and prevents further absorption of the swelling agent.¹⁶² The requirements of paper for vulcanization are in most respects similar to those for any saturating paper, that is, the paper should have an open structure which permits uniform penetration of the swelling agent. Unsized or "waterleaf" papers made from new or old rags are generally used. The rags are prepared and beaten to obtain a sheet which is highly porous but which, at the same time, has considerable strength. In general, the softer the original paper, the harder will be the final product, since soft, porous papers absorb the most chemical.

¹⁶² F. L. Simons, *Paper Trade J.* 90, No. 24: 341-343 (June 19, 1930)

NATURE OF FIBER BONDING

At some time during the beating and refining period, it is customary, when making most grades of paper, to add sizing agents, resins, fillers, starches, dyestuffs, or similar materials to the fibrous furnish in order to develop special properties in the final paper. The use of these agents is an essential part of the papermaking process and is described in subsequent chapters. First, however, the subjects of fiber bonding and sheet formation are discussed. This is not the sequence of operation in the papermaking process, but is used because it is easier to understand sizing, filling, and similar operations if the factors involved in fiber bonding and sheet formation are thoroughly understood.

In the present chapter, the nature of fiber bonding will be discussed. This subject is closely related to the subject of fiber preparation. The two subjects are so closely related that it is impossible to discuss one without the other. In many cases, those factors which increase the amount of "wetting" or fibrillation are the same as those which increase the amount of interfiber bonding.

The nature of interfiber bonding is extremely complex. James Strachan, who has studied the phenomena for many years, said in 1946 that there was little more known then about the precise nature of bonding than there was twenty years before.¹ This may be so, but it does not mean that there has been a lack of interest on the part of paper chemists. The subject is really the fundamental basis of papermaking and consequently warrants considerable thought and study.

Importance of Fiber Bonding

Satisfactory paper cannot be made unless there is a high degree of bonding between the fibers in the sheet. Glass fibers, artificial silk, and asbestos fibers do not produce strong papers because they do not bond to each other. Properly beaten cellulose fibers, on the other hand, are capable of a high degree of interfiber bonding and consequently can be made into strong paper. It is impossible to express the strength of paper in terms of a single factor, because sheet strength is a complex function of fiber length, condition of fiber surface, size of the fibers, orientation of fibers in the sheet, and

¹ J. Strachan, *Paper-Maker* TS 41-42 (May, 1946)

density of the sheet; but of all the single factors which might be used as an expression of sheet strength, the amount of fiber-to-fiber bonding is the most significant.

Deficiencies in the strength of paper must be attributed to deficiencies in bonding, and not to a lack of ultimate intrinsic fiber strength. The tensile strength of paper in the direction of its greatest strength ordinarily amounts to less than 10 to 15% of the theoretical tensile strength which would be obtained if the individual fibers were held together by forces equal to intrafiber bonds.² Thus, it is inaccurate to speak of "fiber strength," as the papermaker often does, since reference is not made to the strength of the individual fibers, but rather to the strength of the paper made from these fibers under certain specified conditions. Individual fiber strength has little or no effect upon this property. When there is a difference between the strength of test sheets made from two different pulps following the same beating procedure, it can be attributed to differences in the physical or chemical properties of the fibers and how these have reacted to affect the degree of interfiber bonding.

Folding, bursting, and tensile strength are some of the physical properties of paper which are most affected by changes in the amount of interfiber bonding. On the other hand, tearing strength is influenced to a considerable extent by fiber length, as well as by the amount of interfiber bonding. Unlike the other strength properties, tearing strength tends to decrease with increased fiber bonding after a minimum amount of bonding has taken place. This can be partly explained by the fact that increased coherence in the sheet tends to concentrate the tearing force into a small area, instead of permitting it to diffuse over a wide path. Cellophane, for example, has a very low tearing strength, once the tear is started, because of its high degree of coherence. In addition to its effect on the above tests, interfiber bonding also reduces surface "fuzz," a condition caused by loose ends of fibers projecting above the surface of the paper. These loose fibers may be present when the sheet is made or they may be produced by friction during use of the paper, but in either case, interfiber bonding is important in minimizing the condition.

Theories of Fiber Bonding

A sheet of dry paper is held together by forces of cohesion which are brought into play during the drying of the sheet. Wet paper is weak, but dry paper is held together by forces which are ordinarily quite powerful. The great strength of these forces is attested by the effort required to rupture the paper and also by the large increase in the density of the sheet which takes place during drying.

² F. T. Carson, *Paper Trade J.* 78, No. 12: 113-118 (March 20, 1924)

Effect of Surface Tension

Surface tension effects are important in bringing the fibers together during the drying of the sheet. As water is removed during drying, surface tension effects create a really tremendous force which compacts and draws the fibers into more intimate contact. To illustrate the intensity of the pressures due to surface tension, Campbell^{3,4} has calculated that two round fibers of 0.003-cm. diameter lying parallel to each other and with a common water contact in the nip between them will be pulled together with a force of nearly 90 p.s.i. If these were smaller fibrils of diameter 0.0002 cm., the pressure would be 540 p.s.i. The compacting force may be the surface tension of water films which are located between the fibers during drying, or it may be a stray force of surface tension which is developed between the interfaces of adjacent fibrillae; but in either event, the force of contraction is dependent on the average fiber diameter. The force of surface tension is so important in fiber bonding that the presence of even small amounts of agents which reduce surface tension will lower the compacting force and result in a sheet of low-density and low-strength properties. Removal of the interfiber water by sublimation at -6°C . so that surface tension forces are no longer a factor results in a considerable loss in sheet strength due to a reduction in fiber bonding.⁵

Types of Bonds

After water is removed and the fibers drawn together by surface tension, another type of force then becomes responsible for holding the fibers together in the dry paper. There are four types of forces which might conceivably be involved in fiber bonding: (1) primary valence chemical bonds, (2) polar bond attraction, (3) hydrogen bonds, and (4) interlocking surfaces. The effect of interlocked surfaces is not of much importance because of the highly elastic and readily compressible nature of cellulose fibers.⁶ Primary valence bonds are also believed to play little or no part, since the forces involved in interfiber bonding are considerably weaker than those which exist between the crystallites in the fiber structure. Chemical bonds require about 30,000 calories per mole for dissociation, whereas polar bond attraction can be dissociated with only about 2,000 calories per mole. The bond between fibers in the average paper can be broken by water which is typical of polar bond attraction.

It is now believed that the predominating force in interfiber bonding is

³ W. B. Campbell, Pulp and Paper Research Inst. of Canada, Lab. Report No. 75 (Oct. 31, 1946)

⁴ W. B. Campbell, *Paper Trade J.* 125, No. 19: 84-86 (Nov. 7, 1947)

⁵ J. E. Jayne, J. C. Tongren and D. T. Jackson, *Tappi* 33, No. 1: 32-35 (Jan., 1950)

⁶ G. E. Landt and S. A. Rulon, *Paper Trade J.* 111, No. 4: 44-48 (July 25, 1940)

one of secondary valence or molecular cohesion between hydroxyl groups of adjacent fibrillae, since a force of the magnitude of secondary valence force is necessary to explain the contraction and increase in density which occur when highly beaten stock is made into paper. The fact that paper can be made under special conditions with a density fairly close to the ultimate (1.56) for cellulose indicates that the association between fibers approaches the limits of molecular dimensions. In sheets of such high density, bonds are formed between the hydroxyls of adjacent fibrillae which can be visualized as establishing a fairly continuous network in the paper. This internal tension, as Campbell calls it, is believed to be principally between the crystallites, and thus belongs in the class of secondary valence forces. Further indication that these forces are of molecular dimension is the high ultimate tensile strength of cellulose sheets. Strengths obtained on paper gelatinized with zinc chloride are in the neighborhood of 18,000 to 20,000 p.s.i., which compares favorably with values of 20,000 to 25,000 p.s.i. for substances such as cast iron, copper, and aluminum, where the structural forces are definitely related to the molecular scheme.⁶ Clark points out that the strongest and most water-resistant bonds are formed between the primary hydroxyl group of one cellulose chain, and either the primary or secondary hydroxyl group of another chain. Fortunately, this is the type of bond most likely to form.

Another factor which determines the strength of the internal bond is the orientation, if any, of the crystallites which are in contact. If these crystallites are lined up in parallel fashion and point the same way, bonding will be at its maximum, because more hydroxyl groups will be brought into contact. This explains the high degree of bonding in cellophane where the crystallites are more nearly parallel than they are in paper.⁷ Landt and Rulon⁸ showed that applying a force of 125 g. per inch on paper gelatinized in zinc chloride increases the strength in the direction of the tension because of a greater orientation of chain molecules in that direction. Campbell's concept of bonding force⁹ calls for a preferred rearrangement of the crystallites as a result of crystallographic forces.

Partial Solubility Theory

Campbell's partial solubility theory is one which has been widely used to explain the mechanism of interfiber bonding. This theory is based upon an earlier hypothesis of Urquhart,¹⁰ which proposed that cellulose is soluble in water in certain stages. The solubility theory, as applied to beaten fi-

⁷ H. de Witt Smith, *J. Textile Inst.* 22: 170-188 (1931)

⁸ G. E. Landt and S. A. Rulon, *Paper Trade J.* 111, No. 4: 44-48 (July 25, 1940)

⁹ W. B. Campbell and L. M. Pidgeon, *Pulp Paper Mag. Canada* 29, No. 6: 185-190 (Feb. 6, 1930)

¹⁰ A. R. Urquhart, *J. Textile Inst.* 20, T 125-132 (1929)

bers, is based upon the supposition that the cellulose crystallites on the surface of the fiber become partially "dissolved" in water and in this state attach themselves to similar crystallites on adjacent fibers. While in this state of near solution, the molecules or crystallites are endowed with a certain freedom and can arrange themselves so that they are pulled together by secondary valence forces when the water is removed. In this way, the fibers are united by the crystallizing of the cellulose during the evaporation of water.

Clark¹¹ regards the surface of well-beaten fibers as a "two-dimensional colloidal system" in which the surface fibrillae have two dimensions in the colloidal range, but are anchored to the fiber in the third. Thus, these fibrillae, which are made up of units at least as thick as cellulose crystallites, act almost as if they were in colloidal solution. The degree of adhesiveness between fibrillae depends on the degree of colloidal solubility, which is inversely proportional to the degree of polymerization of the cellulosic and hemicellulosic material making up the fibrillae. The shorter the chain length, the greater the concentration of this "partially dissolved" material in surface solution.

In many respects, Clark's theory is similar to that of Campbell's. The two theories, taken together, furnish a mental picture of what is meant by "papermakers' hydration." According to these concepts, the surface of the fibers may be visualized as covered by water molecules which are so strongly adsorbed and oriented that they "hydrate" the surface. In support of this theory, Clark¹² showed that a strong bond can be developed between two sheets of cellophane by wetting, pressing, and drying. Since no fibrillation is involved, the cellulose molecules are probably brought into close contact by some sort of "solution" phenomenon.

Strachan's work,¹³ in which he found that small but constant quantities (about 15 p.p.m.) of material are dissolved from purified cotton cellulose by cold water, has also been used as further evidence of the partial solubility theory. In this connection, Kress and Bialkowsky¹⁴ found that the dissolved solids in the beater are increased by beating. Strachan¹⁵ has suggested that this colloidally dispersed cellulose acts to cement the fibers together during interfiber bonding. Clark suggests a similar mechanism in which some fibrillated material in the secondary wall of the fiber may be rubbed off during beating to produce fiber debris which acts as an adhesive

¹¹ J. d'A. Clark, *Paper Ind.* No. 5: 507-510 (Aug., 1943)

¹² J. d'A. Clark, *Paper Trade J.* 97, No. 26: 25-31 (Dec. 28, 1933)

¹³ J. Strachan, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 19: 171 (1938)

¹⁴ O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 35-44 (Nov. 12, 1931)

¹⁵ J. Strachan, *World's Paper Trade Rev.* 109, Convention Number: 54-66 (Mar., 1938)

filler. However, this "free" colloidal or soluble material is at best only a secondary cementing agent in fiber bonding.

Nature of Fiber Surface

The preceding theories lead to the conclusion that the ability of fibers to produce fiber-to-fiber bonding is dependent upon the hydrophilic nature of the fiber surface. The presence of hemicellulosic material increases the hydrophilic nature of the fiber and hence increases the strength per unit area of the bond. High alpha pulps containing nearly 100% true cellulose do not form colloidal solutions on the surface of the fiber and therefore show low interfibrillar adhesion and produce weak papers. The condition of the fiber due to caustic treatment is probably also a factor with high alpha pulps.

Rag pulps are an exception to the above, since they form strong sheets in spite of the relatively high degree of polymerization of the cellulose, but this is due to their unusual structure which causes the fibers to unravel into exceedingly fine fibrils. Cotton linters or hull fiber do not fibrillate in the same way as staple fiber, and hence do not produce as strong papers.¹⁶ Moreover, it has been pointed out that much of the strength of so-called high-strength rag papers is the result of tub sizing, and that very few unsized rag papers are equal to kraft papers in bursting and tensile strength. The work of Musser and Engel^{17,18} indicates that a mild degradation of cotton pulp with acids and oxidizing agents causes the pulp to produce stronger paper than can be made from the undegraded cotton, because the degraded pulp has a more pronounced hydrophilic nature. Some rag pulps have no higher degree of polymerization than bleached sulfite pulps.

With ordinary papers, wetting with water destroys all bonding, because water "dissolves" the cellulose-to-cellulose bonds. For example, a paper sample with a tensile strength of 7.28 kg. in the dry state had a strength of 0.69 kg. when wet with water.¹⁹ On the other hand, wetting with less polar liquids does not reduce the bonding to as great an extent, the preceding sample having a tensile strength of 2.32 kg. when thoroughly wetted with methyl alcohol, and an even higher tensile strength when wetted with higher alcohols. Special wet strength papers retain a high proportion of their strength when wetted with water, but these are bonded with a different type of bond than ordinary cellulose-to-cellulose bonds (see Ch. XII).

Cellulose fibers will not form a strong sheet of paper in acetone or non-

¹⁶ D. M. Musser and H. C. Engel, *Paper Trade J.* 113, No. 2: 13-16 (July 10, 1941)

¹⁷ D. M. Musser and H. C. Engel, *Paper Trade J.* 113, No. 2: 13-16 (July 10, 1941)

¹⁸ D. M. Musser and H. C. Engel, *Paper Trade J.* 114, No. 15: 173-175 (Apr. 9, 1942)

¹⁹ W. B. Campbell, *Tappi* 32, No. 6: 265-271 (June, 1949)

polar liquids. On the other hand, fibers of cellulose acetate or cellulose ether, which are partially soluble in acetone, will form exceptionally strong sheets in this medium,²¹ and cellulose acetate will also form strong sheets in alcohol, since the fibers are partially soluble in this liquid as well. However, neither of these highly substituted cellulose derivatives will produce strong paper when water is used as the dispersing medium because the fibers are not hydrated by water.

Along the same line, Dixon²² has shown that the adsorption of hydrophobic materials or surface-active agents on the surface of cellulose fibers greatly decreases the amount of fiber-to-fiber bonding, probably because these agents are sorbed on the fiber surface in such a way that the large hydrophobic group protrudes from the surface of the fiber and reduces the hydrophilic nature of the fiber surface. The sheet-forming qualities are also reduced by treatment with tannic acid, probably because of a "dehydration" of the fiber surface.

It has been shown by a number of workers^{23,24} that partial replacement of the hydroxyl groups on cellulose fibers by either methyl, ethyl, or acetyl groups increases the sheet strength when the pulp is formed into paper in water. For example, Jayme and coworkers²⁵ were able to increase the bursting strength by 50% through the introduction of 9% methoxyl in the pulp. Fibers having an acetyl content of 5 to 8% also make exceptionally strong paper in water, as shown by Aiken,²⁶ who obtained an 80% increase in the bursting strength of rag pulp by the introduction of 3% acetyl. The introduction of these substituent groups actually makes a greater number of hydroxyl groups accessible for hydration and increases the partial solubility of the fiber surface by forcing apart the cellulose crystallites. However, as would be expected, the substitution can be carried only to a small per cent, since too high a degree of substitution reduces the number of available hydroxyl groups and thus reduces the solubility or hydration of the fiber. Beyond a definite degree of substitution (which is roughly 5 to 6% acetyl or 9% methoxyl groups), the strength of sheets formed in water progressively decreases until the strength reaches almost zero at high degrees of substitution.

Vinyl resin fibers have been suggested for papermaking in spite of their non-polar nature,²⁷ but in this case the bond must be effected by hot calendering of the sheet and not by ordinary methods. Furthermore, with

²¹ J. C. Bletzinger, *Ind. Eng. Chem.* 35, No. 4: 471-480 (Apr., 1943)

²² H. P. Dixon, *Paper Trade J.* 111, No. 3: 29-36 (July 18, 1940)

²³ J. C. Bletzinger, *Ind. Eng. Chem.* 35, No. 4: 471-480 (Apr., 1943)

²⁴ G. Jayme and O. Froundjiam, *Cellulosechemie* 18, No. 1: 9-12 (Jan., Feb., 1940)

²⁵ G. Jayme and O. Froundjiam, *Cellulosechemie* 18, No. 1: 9-12 (Jan., Feb., 1940)

²⁶ W. H. Aiken, unpublished but reported by Clark

²⁷ H. E. Shearer, *Paper Trade J.* 125, No. 14: 157-158 (Oct. 2, 1947)

these fibers it is necessary to add a wetting agent in order to promote wetting of the fibers by water during the cutting treatment and sheet formation. By incorporating 15 to 25% of vinyl resin fiber in the regular fiber furnish, special heat seal papers can be produced which have a special use for tea bags, filter papers, packaging, etc. The paper is said to heat seal at 115 to 130° C. at a pressure of 200 to 300 lb.²⁸

Mineral fibers, e.g., asbestos, can be used in making paper products such as insulation, lining paper, paper covering, and gaskets. These papers are, however, loosely felted and low in strength unless binders such as starch are added. Rock wool fibers, made by dissolving natural limestone rock or industrial slag and blowing into fibers, also makes a very weak product unless binders are added. Synthetic resins are generally used for bonding the fibers together in rock wool products.

Factors Affecting Fiber Bonding

The degree of bonding between the fibers in a sheet of paper depends on the chemical and physical nature of the fiber surface and the manner in which the fibers have been formed into the sheet of paper. It is strongly influenced by the area of the fibers in actual contact and the number of bonds set up in the fibrous structure as a result of beating and sheet formation. The mechanical treatment which the fibers undergo in the beating process is a direct factor affecting the coherence of the fibers in the sheet because of the effect produced on the surface of the fibers. In addition to the effect of beating, interfiber bonding is influenced by certain properties of the pulp itself, such as the amount of lignin, hemicellulosic material, and degraded cellulose present, and the length of the fibers, all of which are determined by the species of wood used and the conditions under which it was cooked and bleached. Both the physical and chemical properties of pulp fibers are important in fiber bonding, and these properties are so interrelated that it is difficult to establish a definite relationship between a single property and the papermaking qualities of a pulp. This is particularly true in the case of the chemical properties, since it is difficult to remove one chemical constituent or group of chemically related constituents without removing or altering some of the other constituents of the pulp.

Effect of Beating

In the preceding chapter, it was pointed out that unbeaten fibers will not form into a strong sheet of paper. There are several reasons for this: (1) unbeaten fibers may be enveloped in a layer which prevents strong adhesion; (2) unbeaten fibers are relatively large in size, which contributes to their stiffness and prevents them from being drawn together during dry-

²⁸ H. E. Shearer, *Tech. Assoc. Papers* 31: 586-588 (June, 1948)

ing; (3) most important, however, is the fact that unbeaten fibers have a very low external specific surface.

One of the first things which may be accomplished in beating is the rupture and partial removal of the primary wall, thereby exposing the secondary wall of the fiber to the beating operation. After this is accomplished, the bruising, rubbing action of the beater causes the fibers to fray out into fine fibrils which increases the amount of exposed surface area of the fibers (see Tables V and VI in Ch. VI) and, at the same time, makes the fibers increasingly flexible and plastic. The increased specific surface obtained on beating increases the magnitude of the surface tension forces drawing the fibers together and also makes it possible for an increased area of fiber surface to come into contact during sheet formation, thereby increasing the adhesion between fibers.

TABLE I
EFFECT OF BEATING ON AREA OF FIBERS IN OPTICAL CONTACT

Beating time (spruce sulfite), min.	Freeness, S-R, cc.	Area con- tributing to S'	Measured specific surface	Area in optical contact	Percentage of area in contact
0	835	8500	11,900	3,400	29
15	690	5600	12,700	7,100	56
30	520	4800	15,300	10,500	69
60	355	4000	16,000	12,000	75

Parsons²⁹ used the difference between the unbonded area of the paper, i.e., the area of the paper not in optical contact, and the total specific surface as a measure of the area in optical contact, an area which is assumed to be equal to the bonded area in the paper. In making the calculations, the silvering technique (see section on specific surface in Chapter VI) was used to measure the total surface of the fibers available for bonding, and the scattering coefficient, S value, from the Kubelka and Munk equation (see optical properties of paper in Chapter XVI) was used to calculate the unbonded area in the paper. This latter calculation was made by assuming that the ratio between the total surface area and the unbonded area of the paper is the same as the ratio between the scattering coefficient of the paper in the completely unbonded state (obtained by forming some of the same pulp into a sheet of paper in acetone or butyl alcohol) and the scattering coefficient of the paper in question.

Using the above method, Parsons obtained the results in Table I showing effect of beating of bleached spruce sulfite on the area of paper in optical contact. These results show that the area of fibers in optical contact increases regularly with increased beating. Using an air permeability method

²⁹ S. R. Parsons, *Paper Trade J.* 115, No. 25: 314-322 (Dec. 17, 1942)

based upon the Kozeny equation, Brown³⁰ found that the area involved in fiber-to-fiber bonding is negligible in handsheets made from unbeaten sulfite pulp. When the same pulp was beaten to a Schopper-Riegler freeness of 610 ml., the exposed fiber surface of the handsheets was only 70 to 75% that of the loose fibers, indicating that only 25 to 30% of the external surface was involved in fiber-to-fiber bonding. Using bleached kraft, Ratliff³¹ found that bursting and tensile strength increased linearly with an increase in bonded area in the early stages of beating, but that the slope of the bonded area-strength curve falls off in the later stages of beating. It was concluded that in the latter region, failure was due to the breaking of intrafiber bonds.

The effects of increased beating on the strength properties of paper has been shown in Figure VI-1. It can be seen from this figure that the tensile and bursting strengths increase with beating, whereas the tearing resistance decreases after a small initial increase.

Effect of Fibrillation

It has been pointed out that the primary wall surrounding the fiber is a deterrent to fiber bonding, and if this layer is present, it is impossible to form a sheet of strong paper, no matter what conditions are used. A slight amount of beating changes this situation, since it removes the primary wall, but even so, strong paper cannot be made from lightly beaten fibers unless tremendously high pressures are applied to the sheet in a wet condition, since great pressure is required to bring the fibers into intimate contact. On the other hand, well-beaten pulp will form readily into a strong sheet with relatively light pressure because of the greater responsiveness of the fibers to the contracting force. This more amenable character of beaten pulp is attributed to the fibrillation which occurs during beating.

On the above basis, it can be seen that fibrillation is important in papermaking, because it permits paper to be made under practical conditions. Equally strong paper could be made from lightly beaten pulp, but unreasonably high pressures would be required which would interfere with other aspects of the sheet formation. Fibrillation may therefore be regarded as an essential function which serves to reduce the effective particle size of the fibers and to permit their compression into a dense sheet of paper under ordinary conditions. Fibrillation is the means by which sheets of high solid fraction are obtained.³² The lack of fibrillation in rayon fibers explains why these fibers will not produce a strong sheet of paper under ordinary conditions in spite of their hydrophilic nature.

In order to illustrate the importance of fibrillation, the steps which oc-

³⁰ J. C. Brown, *Tappi* 33, No. 3: 130-137 (Mar., 1950)

³¹ F. T. Ratliff, *Tappi* 32, No. 8: 357-367 (Aug., 1949)

³² R. H. Dougherty, *Paper Trade J.* 93, No. 2: 39-44 (July 9, 1931)

cur in the drying of paper will be reviewed. In the first step, the forces of surface tension act to bring the fibers closer together. On unbeaten stock, where the fibers are relatively coarse, this force will not be great enough to cause much contraction, but if the stock is well fibrillated, the sheet will shrink extensively on drying, since the fibrils have a low resistance compared with the surface tension forces which are drawing them together.³³ Campbell³⁴ has pointed out that the rigidity of the fiber is proportional to the fourth power of its cross-sectional diameter and, on this basis, unfibrillated fibers are rigid enough to withstand the compacting force of surface tension, but the fine fibrils and fibrillae are not. Thus, the amount of contraction depends upon the fineness of the fibers or, in other words the amount of fibrillation. Furthermore, the total surface tension effect increases greatly with an increase in the fineness of the fibers and fibrillae. As drying continues, the wet sheet continues to contract, due to the fibers being brought closer together, resulting in a reduction in the size of the air spaces and increase in the density of the sheet. The final bonding takes place after the interfibril surfaces come into close enough proximity to be

TABLE II

EFFECT OF BEATING ON SHRINKAGE OF WET PAPER ON DRYING

Time in beater, hours	0	1	2½	4
Freeness (Green), cc.	590	550	270	85
Shrinkage, %	40	55	65	70

under the strong influence of molecular attractions of adjacent hydroxyl groups. During this period, the water of imbibition is forced out and a permanent bond is formed.

There is a difference in the manner of shrinkage, as well as the amount of shrinkage, between beaten and unbeaten fibers. Beaten fibers do most of their contracting before the individual fibers begin to shrink, whereas unbeaten fibers contract very little in this stage of drying.³⁵ Both beaten and unbeaten fibers shrink the same amount after the moisture content is lowered to the point where fiber shrinkage starts, since this involves a contraction of the fibrils within the fiber; but since beaten fibers undergo considerable contraction before the moisture content drops to this level, the over-all amount of contraction is greater in sheets made from well-beaten fibers than it is from slightly beaten fibers. In other words, all fibers shrink after the moisture content drops below their saturation level, but beaten fibers are drawn together considerably before this point is reached. The effect of beating on the over-all shrinkage of wet paper is shown in Table II.³⁶ The

³³ W. B. Campbell, Canadian Dept. of Interior, *Forest Service Bull.* 84, (1933)

³⁴ W. B. Campbell, *Ind. Eng. Chem.* 26, No. 2: 218-219 (Feb., 1934)

³⁵ D. W. McCready, *Paper Trade J.* 95, No. 11: 125 (Sept. 15, 1932)

³⁶ R. H. Doughty, *Paper Trade J.* 101, No. 16: 231-233 (Oct. 17, 1935)

shrinkage which paper undergoes when dried under conditions of zero tension is sometimes used as a measure of the wetness of the pulp, independent of the amount of fiber cutting.

Fibrillation increases the dry strength of paper through its effect in increasing the number of fiber-to-fiber bonds, and consequently, over most of the beating range an increase in fibrillation results in a proportionate increase in the strength of the sheet. However, beyond a certain point further beating results in a decrease in strength. Sheets made from such overbeaten pulp are weaker and possess different characteristics from sheets made from pulp which has been beaten for the optimum length of time, because the gross fiber structure is partially destroyed when the pulp is beaten excessively. Papers made from overbeaten fibers derive too much of their strength from interfiber bonding obtained at the expense of internal fiber strength. Maximum strength is obtained when the fibers are relatively intact, but have a high degree of external or surface fibrillation compatible with longest fiber length.

Effect of Hemicelluloses

In the preceding chapter it was pointed out that pulps which have a high hemicellulose content beat rapidly and form sheets of high strength, whereas pulps with a low hemicellulose content beat with great difficulty and form weak sheets (with the exception of rag pulps). The importance of hemicellulose content in the development of strength properties from wood pulps is now well recognized. The effectiveness of the hemicelluloses is believed to be due to the fact that hemicelluloses have a shorter chain length than true cellulose and are more hydrophilic and, as a result, "wet" better and produce a stronger bond when dried in contact with adjacent fiber surfaces. The fact that the hemicelluloses function as a binder through the mutual bonding of their hydroxyl groups has been demonstrated by Aiken,³⁷ who showed that the addition of xylan to regular rag stock greatly increases the strength, whereas the addition of acetylated xylan decreases the strength, because it has no effective hydroxyl groups. The true cellulose is itself hydrophilic by nature, but part of it is bound in a rigid crystalline structure which is not available for hydration, and even the remaining amorphous cellulose is not readily hydrated if the chains are long. Another reason for the effectiveness of hemicellulosic material in fiber bonding is that it introduces points in the fiber structure where it is easier for fibrillation to take place.

It should be pointed out that it is not the entire hemicellulose fraction which is effective in fiber bonding, nor is it the total pentosan content. The fact that soda hardwood pulps have a higher pentosan content than softwood

³⁷ W. H. Aiken, *Ind. Eng. Chem.* 35, No. 11: 1206-1210 (Nov., 1943)

sulfite pulps and yet do not "wet" as well indicates that pentosans as a group are not effective. Cottrall³⁸ has shown that the bursting strength of bleached wood pulps follows very closely the gamma cellulose content of the pulp, irrespective of whether the pulp is a sulfite or sulfate pulp, although there must be other favorable factors, such as adequate fiber length and minimum of fiber degradation. Table III was taken from his published re-

TABLE III

RELATIONSHIP BETWEEN BURST RATIO AND ALPHA, BETA, AND GAMMA
CELLULOSE CONTENTS OF BLEACHED PULPS

Type of pulp	Alpha cellu- lose, %	Beta cellu- lose, %	Gamma cellu- lose, %	Burst ratio ^a	Cupram- monium viscos- ity ^a
Very strong Scandinavian bleached sulfate	87.6	0.03	12.4	2.25	29.5
Very strong Scandinavian bleached sulfite	87.9	0.9	11.2	1.55	45.5
Semibleached sulfate	89.2	1.7	9.1	1.45	13.1
Strong U. S. West Coast bleached sulfite	89.1	1.9	9.0	1.30	25.7
Fairly strong U. S. bleached sulfite	90.4	1.6	8.0	1.20	46.5
Typically refined rayon pulp	91.5	2.7	5.8	0.90	24.2
Special rayon pulp	90.0	5.8	4.2	0.64	13.2
Special alpha pulp (for acetylation)	94.6	2.1	3.3	0.75	22.3

^a After beating to 300 Canadian freeness.

sults, where it can be seen that burst increases as the gamma cellulose is increased. Greenane³⁹ also found a marked relationship between gamma cellulose content and strength, but Hebbs⁴⁰ points out that this relationship does not always hold, particularly when comparing raw and well-cooked pulps. Cottrall⁴¹ himself points out that the relationship does not hold for unbleached pulps because of the presence of significant amounts of lignin which obscure the relation between gamma cellulose and bursting strength. Ratliff⁴² obtained a better correlation between strength (bursting and tensile) and yield in the range of 42 to 50.5% than between strength and hemi-cellulose content in the case of kraft pulps bleached with chlorite.

Klingstedt⁴³ found that the maximum strength of papermaking pulps

³⁸ L. G. Cottrall, *Paper-Maker* 105, No. 5: TS 25-31 (May, 1943)

³⁹ F. J. Greenane, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 25: 220-224 (1944)

⁴⁰ L. G. Hebbs, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 25: 224-228 (1944)

⁴¹ L. G. Cottrall, *Paper-Maker* 105, No. 5: TS 25-31 (May, 1943)

⁴² F. T. Ratliff, *Tappi* 32, No. 8: 357-367 (Aug., 1949)

⁴³ F. W. Klingstedt, *Svensk Papperstidn.* 40: 412-416 (1937)

increases with an increase in the amount of alkali-soluble material in the pulp rather than with the pentosan content. Wise⁴⁴ also points out that the amount of alkali-extractable hemicellulose is more indicative than the total hemicellulose content, using as an example two pulps (aspen bleached kraft and modified "holocellulose") which had the same xylan content but different total alkali-extractable hemicelluloses. The modified "holocellulose," which had the greater alkali-extractable portion, beat more rapidly and produced sheets of higher bursting strength (but lower tear) than the aspen bleached kraft. This coincides with Hägglund and Webjorn's statement⁴⁵ that it is the low-polymerized polyoses which are responsible for easy beating.

The above explains in part why soda pulps do not "wet" as readily as sulfite pulps when the same species is used, because the alkali in the soda process removes the alkali-soluble hemicelluloses, which, as pointed out in the chapter on fiber preparation, causes the fibers to be brittle and fragmentize on beating instead of developing "wetness." It has been said that about one-half of the hemicelluloses in commercial pulps are "manufactured," i.e., they are degraded residues from materials present in the alpha cellulose fraction, and these are not as effective for papermaking as the polyuronides.⁴⁶ Of the cellulosans, mannan has been reported as being more effective than xylan.⁴⁷

Pulps from wheat straw, cornstalks, and other non-woody plants have a much higher hemicellulosic content than wood pulps, but it is important to realize that this alone does not make them perfect as pulps for papermaking. In these plants the dimensions of the fiber, the ratio of fibrous to non-fibrous cells and the physical properties of the fiber are much more important than the chemical properties of the pulp. For example, although the short pithy cells are the ones highest in hemicellulose content, it is the bast fibers which contribute most to the strength because of their greater length and greater capacity for fibrillation. These pulps, being high in hemicelluloses, "wet" up very rapidly so that their use is limited to those papers where the mechanical treatment can be very mild. If the mechanical treatment is not carefully controlled, the pulp becomes very slow to drainage, resulting in slow machine speeds and weak, brittle paper. There are, however, several grades of papers where these fibers are beneficial either by rendering a sheet rigid, such as for corrugating medium, or by lowering the cost of the fiber furnish.

⁴⁴ L. E. Wise, *Paper Ind.* 29, No. 6: 825-829 (Sept., 1947) reporting on unpublished work of R. E. March

⁴⁵ E. Hägglund and B. Webjorn, *Svensk Papperstidn.* 52, No. 6: 131-137 (Mar. 31, 1949)

⁴⁶ TAPPI Monograph No. 6, *Nature of the Chemical Components of Wood*, p. 91. Technical Assoc. of the Pulp and Paper Industry. New York, N. Y. (1948)

⁴⁷ K. G. Jones and E. Rieth, *Wochbl. Papierfabr.* 68: 853 (1933)

Pulp which contains too much hemicellulose hydrates too rapidly and loses freeness before adequate strength is developed, producing a paper which is translucent, rattly, and low in strength. Jayme⁴⁸ found that holocellulose, which contains all the hemicelluloses and no lignin, produced sheets of low strength, but removal of part of the hemicelluloses by weak alkali increased the strength to an optimum value beyond which further removal caused a decline in strength. He found the optimum strength was obtained at a yield of approximately 50 to 52% of the weight of the original wood, although this varied from 56% for the bursting and tensile strengths to 47% for the tearing resistance. Using beech cooked by a mild sulfite cook and bleached with chlorite, Jayme and coworkers⁴⁹ found that the pulp with the greatest over-all strength had the following properties:

Yield	50 to 52%
Alpha cellulose	80.9%
Lignin	1.09%
Hemicelluloses	18.0%

Klauditz⁵⁰ found that raw spruce sulfite pulp bleached with chlorite and then extracted with 0.1% sodium hydroxide increased in tensile strength after extraction at the same time that the yield decreased from about 65 to 54%. Ritter and Hajny⁵¹ recognized the value of controlled hemicellulose content and suggested that holocellulose be used as the base from which a pulp with controlled beating properties be obtained. By using prepared holocellulose, degradation of the cellulose during cooking is avoided, and the amount of the rapidly wetting hemicelluloses can then be controlled by extraction with alkali. By this method it is possible to regulate the ratio of true cellulose and hemicellulose and thus obtain a pulp which produces strong paper, but so resists rapid hydration that only a gradual drop in freeness occurs during the beating process.

Other investigators working in other fields have found that there is an optimum hemicellulose content for maximum sheet strength. Obermanns⁵² added xylan, which had been obtained by extracting soda pulp with alkali, in paste form to rag stock, and found that the tearing resistance and folding endurance increased up to an addition of 6.5%, after which the strength decreased with higher percentage. However, the tensile strength increased as a direct function of the pentosan content. When added to purified sulfite pulp, the burst, fold, tear and tensile all increased up to about 16% added

⁴⁸ G. Jayme, *Papier-Fabr.* 40, No. 36: 137; No. 37: 145 (1942)

⁴⁹ G. Jayme and E. Lochmuller-Kerler, *Holz als Roh- und Werkstoff* 5, No. 1: 10-19 (Jan., 1942)

⁵⁰ W. Klauditz, *Papier-Fabr.* No. 7: 247 (Oct., 1943)

⁵¹ G. J. Hajny and G. J. Ritter, *Paper Trade J.* 111, No. 22: 281-284 (Nov. 28, 1940)

⁵² H. E. Obermanns, *Paper Trade J.* 103, No. 7: 109-117 (Aug. 13, 1936)

hemicellulose. When added to regular sulfite pulp, the strength increased up to about 20% hemicellulose, after which the strength properties showed a tendency to drop off slightly. Wise^{53, 54} reports in work on aspen holo-cellulose that the optimum hemicellulose content for maximum bursting and tensile strengths is about 20%. However, at about this point the sheet has minimum opacity and tearing strength which emphasizes that the optimum hemicellulose content depends on those sheet properties desired. The optimum hemicellulose content also depends, of course, on the type of wood and method of cooking.

Effect of Cellulose

Fiber bonding is a highly complex phenomenon which is dependent upon a number of different factors. Among the important ones already mentioned are the amount and type of fibrillation and the amount of hemicellulose or degraded cellulose that is present in the fibers. It has been shown that fiber bonding increases as the amount of hemicellulosic material is increased up to a certain point, but that beyond this point, a further increase lowers the folding and the bursting strengths. So far, however, nothing has been said about the importance of the true cellulose component of the fiber. This section is concerned with the relationships that have been noted between sheet strength and the degree of polymerization of the true cellulose in the pulp fibers.

The effect of the true cellulose on fiber bonding is difficult to evaluate, inasmuch as it is difficult to obtain a reliable indication of the degree of polymerization of cellulose. The cuprammonium and cupriethylenediamine viscosity tests are widely used for this purpose, but these tests have definite limitations, since they are affected by the amount of lignin and hemicellulosic material present in the pulp, as well as by the state of the true cellulose. For this reason, viscosity tests cannot be used as an absolute indication of the degree of polymerization of the cellulose.

Within certain limits, there appears to be a relationship between the degree of polymerization of the cellulose in pulp fibers (as measured by the viscosity test) and the strength of paper made from the fibers. This relationship is not always valid (see Table III), and the viscosity test is not widely used in the industry to any extent as a guide to fiber bonding. However, there appears to be sufficient relationship under certain circumstances to warrant attention.

Among the many investigators who noted a relationship between D.P.

⁵³ TAPPI Monograph No. 6, *Nature of the Chemical Components of Wood*, p. 92. Tech. Assoc. of the Pulp and Paper Ind., New York, N. Y. (1948)

⁵⁴ L. E. Wise, *Paper Ind.* 29, No. 6: 825-829 (Sept., 1947) reporting on unpublished work of R. E. March

of the pulp and the strength-producing qualities of the pulp was Jayme,⁵⁵ who found that the tearing and bursting strength increased almost directly when the D.P. of the pulp was increased from 400 to 1400, and that the folding endurance increased greatly after a D.P. of 900. Staudinger and Reinecke⁵⁶ obtained substantially the same results in that they found that tearing resistance and bursting strength increased as the D.P. increased up to about 1000, after which the strength became nearly constant. Pascoe⁵⁷ found a correlation to exist between cuprammonium viscosity and bursting strength for unbleached sulfite pulps, but no correlation with tearing strength, although he found a correlation between tear and viscosity when bleached sulfite pulps were used. Jayme⁵⁸ noted that there was less relationship between D.P. and strength properties in the case of unbleached pulps than in the case of bleached pulps. Rulon⁵⁹ noted a progressive decrease in the maximum bursting strength of sulfite and alkaline cooked pulps as the cuprammonium viscosity was lowered through bleaching. On the other hand, Parsons⁶⁰ has shown that the folding endurance and burst of sulfite pulps increased with increased fluidity (reciprocal of cuprammonium viscosity) due to bleaching. However, this increase in strength with decreasing viscosity occurred only up to the time that the pulp was completely bleached, after which the pulps lost strength due to overbleaching. Musser and Engel⁶¹ noted that when the specific viscosity (0.5% in cuprammonium) of cotton pulp is reduced below about 10, there is a significant decline in the physical properties of the paper, and this occurs at about the same point that the beating rate is increased. Landt and Rulon⁵⁹ found that cotton pulps of low viscosity produced papers of low tensile strength. McGregor⁶² degraded rag pulps with acids, bleach, and heat to cuprammonium viscosities representing two-thirds, one-half, and one-third of the original values and noted a definite relation between viscosity and maximum folding endurance. Bialkowsky⁶³ also showed that the fold test decreased simultaneously with a decrease in the cuprammonium viscosity of rag pulps.

Schur and Lewis⁶⁴ have furnished information on the relationship

⁵⁵ G. Jayme, *Papier-Fabr.* 40, No. 36: 137; No. 37: 145 (1942)

⁵⁶ H. Staudinger and F. Reinecke, *Holz als Roh- und Werkstoff*, No. 9: 321-323 (Sept., 1939); *Papier-Fabr.* 36, No. 49: 489-495 (Dec. 2, 1938)

⁵⁷ T. A. Pascoe, *Tech. Assoc. Papers* 30: 422-426 (June, 1947)

⁵⁸ G. Jayme, *Cellulosechemie* 21, No. 4: 73-86 (Sept., 1943)

⁵⁹ G. E. Landt and S. A. Rulon, *Paper Trade J.* 111, No. 4: 44-48 (July 25, 1940)

⁶⁰ J. L. Parsons, *Paper Trade J.* 93, No. 1: 42-44 (July 2, 1931)

⁶¹ D. M. Musser and H. C. Engel, *Paper Trade J.* 113, No. 2: 13-16 (July 10, 1941)

⁶² G. H. McGregor, *Paper Trade J.* 102, No. 11: 155-167 (Mar. 12, 1936)

⁶³ H. W. Bialkowsky, *Paper Trade J.* 90, No. 11: 53-58 (Mar. 13, 1930)

⁶⁴ M. O. Schur and H. F. Lewis, *Tappi* 33, No. 8: 392-397 (Aug., 1950)

which exists between the degree of polymerization of pulp as measured by the cupriethylenediamine viscosity test and the beating qualities and strength-producing qualities of the pulp. According to their information, high-viscosity pulps (30 cp. or higher, D.P. about 1500) are characterized by high resistance to cutting so that by the time the fibers are reduced to the proper length, they are sufficiently well fibrillated to produce a strong paper. On the other hand, pulps of very low viscosity (4 cp., D.P. about 600) are easily cut and broken, because of their low tensile strength, and consequently, there is not sufficient opportunity to develop enough fibrillation for producing a strong paper. Therefore, pulps of high viscosity are desirable for papers requiring high strength and high density, for example, filter papers, carbonizing tissues, condenser papers, and currency papers, whereas low-viscosity pulps are desired for papers which require a high degree of softness and bulkiness, for example, book papers.

TABLE IV

CUPRAMMONIUM VISCOSITY VALUES FOR DIFFERENT GRADES OF PAPER

Paper grade	Type of pulp used	Viscosity range	
		Unbleached	Bleached
Glassine	Sulfite	3000-5000	500-1000
Bond	Sulfite	300-1000	45-200
Mimeograph	Sulfite	100-500	25-125
Glassine	Sulfate	500-1500
Wrapping and bag	Sulfate	100-1000	20-100
Book	Soda	5-50	1-10

The above observations lead to the conclusion that when all other conditions are equal, the higher the degree of polymerization of the cellulose in the pulp, the greater the strength of the paper made from the pulp. The relation between strength and D.P. appears fairly valid for cotton pulps (probably because of their less complicated nature), but the relationship is of value for wood pulps only when comparing pulps of the same type, and even then the results are often more affected by some other condition. Sulfate pulps are generally stronger than sulfite pulps at equal or lower D.P.,^{65, 66} and this must be due to other factors which overshadow the effect of the true cellulose component of the fibers. Typical cuprammonium viscosity values for several different grades of paper are shown in Table IV,⁶⁷ where it can be seen that papers of higher density and higher strength tend to have the higher viscosity.

⁶⁵ L. G. Hebbs, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 25: 224-228 (1944)

⁶⁶ J. E. Atchison, *Paper Trade J.* 116, No. 22: 243-254 (June 3, 1943)

⁶⁷ E. D. Rich, *Paper Trade J.* 112, No. 6: 63-68 (Feb. 6, 1941)

Effect of Fiber Length

In the past, paper chemists believed that fiber length played a decisive role in determining the strength of paper, and for many years fiber length was regarded as the most important measure of fiber quality. Fiber length is an exceedingly important index of fiber quality, but it is subordinate to the wetting or fibrillating qualities, since adequate sheet strength can be obtained only by means of a high degree of fiber-to-fiber bonding, which prevents the fibers from slipping past one another. For example, Northern European kraft pulp usually produces paper with higher bursting strength (but lower tear) than kraft pulp from the southern areas of the United States, although the latter has the greater fiber length. As further proof, it has been shown⁶⁸ that the bursting strength of straw pulps, which have an average fiber length between 0.30 to 0.46 mm., may approach under special conditions the bursting strength of spruce pulps having a comparable average fiber length between 1.2 to 1.8 mm. Another indication is that beating increases the bursting, tensile, and folding strengths, even though it tends to decrease the length of the fibers.

In spite of its subordination to fiber bonding qualities, fiber length is a property to be considered in papermaking, because after as much fiber-to-fiber bonding as possible has taken place, the strength of the paper depends principally upon the length of its component fibers. The longer the fibers, the less chance there is for slippage between the fibers when the sheet is subjected to stress. Furthermore, it is generally true that the greater the fiber length, the greater the opportunity for fibril formation, so that pulps which possess fiber length generally have a high capacity for interfiber bonding. Manila makes one of the strongest papers because it has both great fiber length and a high capacity for fibrillation. For the same reason, hydrophilic binders such as starch are more effective the longer the fibers, that is, the effectiveness increases in going from groundwood to soda to sulfite to rag pulp, because the starch furnishes approximately the same fiber-to-fiber bonding on each of these pulps and thereby makes it possible for the factor of fiber length to become predominant. However, as just pointed out, some long-fibered pulps such as manila wet exceptionally well, and for long-fibered, well-fibrillated stock of this type, starch has relatively little influence on strength.

There is a notable lack of agreement among investigators as to the influence of fiber length on sheet properties. Part of this trouble has been caused by the influence of variables which were not kept constant, and part is due to the fact that these findings have been made over a wide space of years and under different backgrounds of knowledge. The various methods

⁶⁸ G. Jayme, *Papier-Fabr.* 40, No. 36: 137; No. 37: 145 (1942)

of determining and reporting average fiber length vary widely (see Ch. VI), and this, of course, affects the conclusions made on the basis of fiber length. The usual method has been to classify a given pulp into fractions of different average length. The difficulty with this method of approach is that fractionation not only separates a pulp into different length fractions, but also gives a complex separation of the fine and coarse fibers, and does not eliminate variables such as differences in the chemical properties of the fiber fractions and differences in the density of test sheets. Another method is to cut a given lot of fibers into fractions of various sizes, and in this connection Brown⁶⁹ found that long fibers which have been cut to the same length as the fines do not produce the same effect as the original fines, thereby attesting to the unique effect of the fines. For one thing, he found that mechanically prepared "fines" do not produce any appreciable slowing of the stock compared with the tremendous slowing obtained with the original fines. Since the original fines are much higher in resin content and ash than the longer fibers, they would be expected to have a unique effect on sheet properties, and this, as mentioned above, has been borne out in fact.

Doughty⁷⁰ fractionated spruce and black gum sulfite by wet screening into long-fibered and short-fibered portions, the mean length for the long-fibered fractions being 2.0 mm. for the spruce and 1.51 for the gum, and the mean length for the short-fibered fraction being 0.2 mm. for the spruce and 0.07 mm. for the gum. His results indicate that tensile strength was not appreciably affected by fiber length as long as the solid fraction of the paper was held constant and, in fact, at constant wet pressing, the short-fibered pulp produced the paper of higher tensile strength because the solid fraction was higher. However, tearing resistance was appreciably higher for the papers made from the long-fibered stock even at the same solid fraction.

Using bleached sulfite fibers cut to different sizes, Brown⁶⁹ found that "manufactured" short fibers produce papers almost devoid of bursting strength, but that the original fines in the pulp produce papers of exceptional bursting strength. The long fibers produce sheets which are relatively low in bursting strength, but are exceptionally high in the matter of tearing resistance.

Clark⁷¹ used viscose artificial silk cut with a sharp guillotine into fractions of 0.5 to 1 mm., 1.5 to 2.0 mm., 2.5 to 3 mm., 3.5 to 4.0 mm., and 4.5 to 5.0 mm., and made papers from these various fractions using locust bean gum as a binder. He found that burst, under these conditions, is propor-

⁶⁹ R. B. Brown, *Paper Trade J.* 95, No. 13: 145-147 (Sept. 29, 1932)

⁷⁰ R. H. Doughty, *Paper Trade J.* 94, No. 9: 114-119 (Mar. 3, 1932)

⁷¹ J. d'A. Clark, *Paper Trade J.* 115, No. 26: 328-334 (Dec. 24, 1942)

tional to the weighted average fiber length (L) and that the various strength properties can be expressed as a function of fiber length as follows:

$$\begin{aligned}\text{Burst factor} &= k_1 L \\ \text{Breaking length} &= k_2 L^{1/2} \\ \text{Rigidity factor} &= k_3 L^{1/2} \\ \text{Tear factor} &= k_4 L^{3/2}\end{aligned}$$

Work on the relationship between pulp properties and fiber length has been done by de Montigny and Zborowski,⁷² using the de Montigny grid for measuring fiber length. In their work they used a bleached sulfate pulp which was beaten to various degrees to vary the fiber length. The results of this work indicate that there is a simple straight-line relationship between the fiber length index of the pulp and the tearing strength of the paper. Bursting and tensile strengths were found to be more complex functions involving both fiber length and slowness.

In general, it might be stated that tearing resistance and, to a lesser extent, folding endurance are basically dependent upon fiber length. In comparison, bursting and tensile strength are more affected by fiber bonding than by fiber length. Vincent and White⁷³ believe that fiber length in the case of chemical wood pulps plays an important part only when the fibers are greater than 0.3 mm. in length. They believe that the bursting strength, tensile strength, and folding resistance tend to increase as the average fiber length is increased from 0.3 to 0.9 mm., and then to decrease with further increase in fiber length. However, tearing strength tends to increase with fiber length indefinitely.

Considerable work has been done on the effect of fineness of fibers in groundwood pulps, since this is one of the most important variables in this type of pulp. Fines from groundwood are different from the fines of chemical pulps, since they tend to be fairly uniform in chemical composition, whereas the fines in chemical pulps contain a comparatively high percentage of ray cells which differ from ordinary cells in their chemical properties. Thus, the effect of fines would be expected to be different for groundwood pulps than for chemical pulps, and most of the work which has been done indicates that this is so. Parsons⁷⁴ noted that the fines from chemical (sulfite) pulps produce sheets which are dense, "tinny," and brittle, whereas the fines from groundwood produce papers which differ little from papers made from the other fractions of groundwood. Kress and Brainerd⁷⁵ fractionated various chemical and groundwood pulps by wet screening and found that

⁷² R. de Montigny and P. Zborowski, *Tech. Assoc. Papers* 29: 226-232 (June, 1946)

⁷³ G. P. Vincent and J. F. White, *Paper Ind.* 27, No. 7: 1038-1039 (Oct., 1945)

⁷⁴ S. R. Parsons, *Paper Trade J.* 115, No. 25: 314-322 (Dec. 17, 1942)

groundwood pulps show increasing burst and tensile strengths as the fiber length and width are decreased, but chemical pulps show the opposite. Schafer and Carpenter⁷⁶ found that the density and physical properties (modulus of elasticity, modulus of transverse strength, and modulus of rupture) of paperboards made from groundwood pulps increased with a decrease in the average fiber length obtained by wet screening the pulp into fractions of different fiber length. Using eastern hemlock groundwood which had been classified by screening into different fractions by weight, Schafer and Santaholma⁷⁷ found that the tearing and bursting strength went through a maximum at an average fiber length of about 0.15 mm. (calculated from the average screen openings for the two screens between which the

TABLE V
EFFECT OF FINES ON PROPERTIES OF GROUNDWOOD PAPERS

	Pulp A			Pulp B		
	Entire pulp	Pulp retained on 35-mesh	Pulp retained on 150-mesh	Entire pulp	Pulp retained on 35-mesh	Pulp retained on 150-mesh
Specific volume	2.2	2.8	2.6	2.2	2.8	2.5
Burst factor (metric)	16.8	9.8	10.2	13.0	6.5	7.1
Breaking length (<i>M</i>)	3300	1830	1870	3100	1350	1750
Tear factor (metric)	39	44	42			
Drainage time (sec.)	51.0	5.2	5.5	16.0	5.5	6.0
Per cent of pulp tested	100	23.1	31.9	100	27.4	34.3

fraction is obtained), whereas the tensile strength increased quite regularly with increases in fiber length following the increase in density of the sheets. It should be pointed out that although this range of fiber length is probably applicable to groundwood pulps, the range is much lower than that indicated as optimum for chemical pulps. Clark⁷⁸ points out the beneficial effect which the fines have on the strength of groundwood papers. Using data obtained from Klem, which is given in Table V, he shows that papers containing all the fines are much higher in burst and breaking length (and the pulp is much "slower") than papers made from fractions from which the fines had been separated. He points out that the "quality" of the fines is more important than the quantity.

⁷⁵ O. Kress and F. W. Brainerd, *Paper Trade J.* 98, No. 13: 163-168 (Mar. 29, 1934)

⁷⁶ E. R. Schafer and L. A. Carpenter, *Paper Trade J.* 91, No. 3: 27-32 (July 17, 1930)

⁷⁷ E. R. Schafer and M. Santaholma, *Paper Trade J.* 97, No. 19: 224-229 (Nov. 9, 1933)

⁷⁸ J. d'A. Clark, *Paper Trade J.* 110, No. 9: 121-124 (Feb. 29, 1940)

The ideal furnish for many papers would contain fibers of all gradation in particle size from the maximum down to the smallest fiber fragments since in this way better packing and higher solid fraction would be obtained in the sheet. The fibers in chemical wood pulps range from about 20 to 35 microns in diameter, and hence do not pack very closely, but the fiber debris created during beating tends to fill in the interstices between the longer fibers and thus produce a stronger and more level sheet.⁷⁹ Using the product of tear resistance and tensile strength as an indication of the quality of groundwood pulps, Vilars⁸⁰ found the ideal mixture to consist of 40 to 45% long fibers, 20% short fibers, and 35 to 40% fines. It is probable that the greater retention of fines in laboratory sheet machines is partly responsible for the greater strength of laboratory test sheets compared with mill paper, particularly in the case of groundwood pulps. It is known that short-fibered hardwood pulps can be added to long-fibered softwood pulps without an appreciable loss in bursting strength, particularly if the hardwoods are cooked by the neutral semichemical sulfite process. Short-fibered hardwoods added in this way increase the density of sheets made from the longer softwood fibers, and thus reduce the amount of beating which is required to obtain a sheet of the same density. Bray⁸¹ reports that under certain conditions a 50-50 mixture of pine and hardwood species (both cooked by the sulfate process) produces a pulp with strength values about equal to the pine pulp alone, with the exception of tearing resistance. As a further example, it can be shown that the blending of such pulps as groundwood and sulfite often gives results which are proportionately better than would be expected, due to the increase in sheet density which is brought about by the groundwood pulp. The relationship which exists between long and short fibers is well illustrated in fiberboards which normally consist of different ratios of long and short fiber fractions. The long fibers act as beams or girders in the board and are principally responsible for the structural or impact strength of the board.⁸² On the other hand, the short hydrated fibers act as the cementing agent and consequently tend to increase the density and the flexural and tensile strengths.^{82,83}

Effect of Lignin

Commercial pulps range in lignin content from about 1.5% for "soft" chemical pulps, about 8% for "hard" chemical pulps to about 16% for semichemical pulps. The effects of lignin on the strength of the final paper is

⁷⁹ J. d'A. Clark, *Paper Trade J.* 104, No. 8: 118-120 (Feb. 25, 1937)

⁸⁰ J. Vilars, *Chimie et Industrie* 5342 (1945), through *C. A.* 40, 2299 (1946)

⁸¹ M. W. Bray, *Paper Trade J.* 120, No. 21: 212-214 (May 24, 1945)

⁸² E. C. Lathrop and T. R. Naffziger, *Paper Trade J.* 127, No. 27: 540-545 (Dec. 30, 1948)

⁸³ E. C. Lathrop and T. R. Naffziger, *Tappi* 32, No. 2: 91-96 (Feb., 1949)

difficult to determine, since it is almost impossible to change the lignin content of pulp fibers without changing some of the other constituents. It is not possible, for example, to use the degree of cooking or bleaching as an indication of the lignin content, since these operations remove not only the lignin but also the hemicelluloses and degraded celluloses, and moreover, these operations tend to degrade the true cellulose component of the fibers. Consequently, the strength properties are affected in different ways, and it is easy to see why there is no positive relationship between the strength characteristics of a pulp and the degree to which it has been cooked or bleached, although there are, of course, well-known qualitative relationships.

In general, lignin affects the properties of pulp in an adverse manner. Pulps with too high a lignin content are slow beating and show poor inter-fiber bonding, and as a result, produce sheets of low density and inferior strength. One exception is stiffness, which is usually increased by the presence of lignin. Jayme^{85,86} believes that the presence of lignin always tends to lower the bonding strength, and he found it difficult to form sheets at all with chemical pulps that contained 12 to 19% lignin. When the lignin was removed with sodium chlorite, the tensile and tearing strength increased steadily, although the folding endurance remained low until the lignin content was reduced below 5%. Similarly, Ratliff⁸⁷ found that kraft pulps (slash pine) which were delignified with chlorite increased continuously in burst and tensile strength through the yield range of 50.5% to 42.0%; tear passed through a maximum at about 46% yield. Along the same line, Simmonds and coworkers⁸⁸ found that it was possible by removing an appreciable quantity of lignin from semichemical hardwood pulp by chlorination to increase the bursting and tearing strengths by 19%, the tensile strength by 10%, and the folding strength by 100%. An appreciable amount of water-soluble hemicelluloses were removed at the same time as the lignin.

Harlow and Fowler⁸⁹ showed by means of microdissection experiments that the cohesion between fibers in paperboards (kraft) increased as the lignin content of the fibers is lowered. At high lignin content, the fibers tend to pull apart with their secondary walls intact, indicating that the inter-cellular lignin prevents good adhesion between the fiber surfaces. However, as lignin is removed, the fiber walls make increasingly better contact, and at very low percentages of lignin, the cohesive force between adjacent fiber

⁸⁵ G. Jayme, *Papier-Fabr.* 40, No. 36: 137; No. 37: 145 (1942)

⁸⁶ G. Jayme and R. Wettstein, *Papier-Fabr.* 36, No. 49: 519-531 (Dec. 2, 1938)

⁸⁷ F. T. Ratliff, *Tappi* 32, No. 8: 357-367 (Aug., 1949)

⁸⁸ S. A. Trivedi, R. M. Kingsbury and F. A. Simmonds, *Paper Ind.* 29, No. 10: 1443-1453 (Jan., 1948)

⁸⁹ W. F. Fowler and W. M. Harlow, *Paper Trade J.* 114, No. 14: 161-162 (Apr. 2, 1942)

walls becomes great enough that the rupture takes place within the secondary wall. Bailey⁹⁰ found that the removal of lignin from already formed fiberboards containing a high lignin content caused virtually no change in the strength properties, thereby indicating that lignin is not involved in interfiber bonding. The relatively low density of groundwood papers compared with papers made from chemical pulps is partly due to the greater stiffness of the lignified groundwood fibers and partly due to their poor bonding qualities.⁹¹

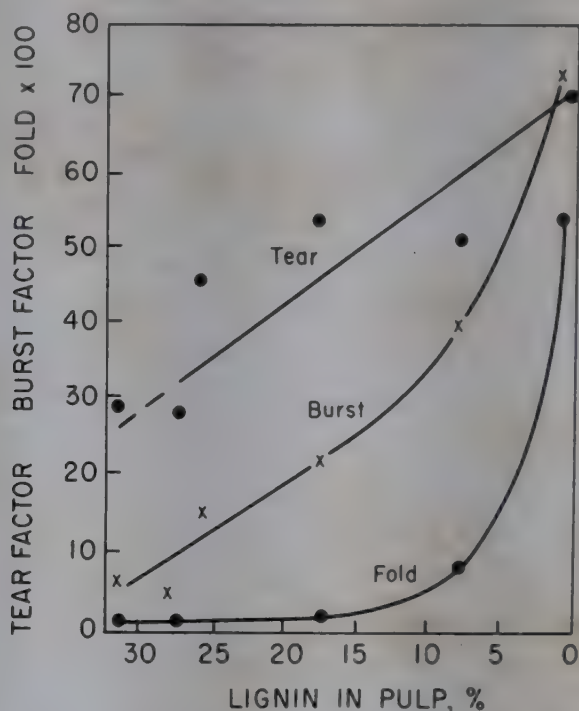


Fig. VII-1. Effect of lignin content on strength of handsheets made from white pine groundwood. Pulps classified in Bauer classifier and extracted with chlorine dioxide in aqueous pyridine solution.

The experiments of Jahn and Holmberg⁹¹ are very interesting. They used groundwood pulps classified according to fiber length to eliminate this variable and used chlorine dioxide as the delignifying agent to minimize attack on the cellulose. Following this procedure, they obtained a rapid and fairly regular increase in bursting strength, tensile strength, tearing resistance, and density of the paper as the lignin content of the pulp was lowered from 27.4 to 1.1%. During this lignin removal, the pentosan content remained relatively constant, and there was little or no fiber degradation. Some of the results are shown in Figure VII-1.⁹¹

The above-mentioned experiments were carried out under special conditions in an attempt to minimize other changes aside from lignin removal. In commercial cooking, however, conditions are quite different, since the re-

⁹⁰ A. J. Bailey, *Paper Ind.* 19: 1273-1276 (1928)

⁹¹ E. C. Jahn and C. V. Holmberg, *Paper Trade J.* 114, No. 17: 203-208 (Apr. 23, 1942)

removal of other substances may overshadow the removal of lignin. For example, it is possible that the removal of lignin in commercial pulping is overshadowed by the simultaneous removal of hemicelluloses. Thus, when the lignin content is lowered below a supposedly optimum value, any loss in strength might very well be caused by the simultaneous removal of hemicellulosic material, and under these circumstances, the true significance of lignin would not be manifested. However, Limerick and Corey⁹² point out that lignin content of fibers exerts an influence on sheet density which surpasses by far the influence of the hemicellulose content.

As mentioned above, Jahn and Holmberg⁹¹ used chlorine dioxide for removing the lignin, but similar increases in strength were obtained when they removed the lignin from groundwood (aspen) by cooking by the soda process for periods ranging from one to four hours. On the other hand, when groundwood (white pine) was cooked by the sulfate process, a maximum in burst, tensile and folding strengths occurred at a lignin content of 6.5%, after which the strength rapidly decreased with further delignification. This loss in strength at lignin contents lower than 6.5% is believed to be due to degradation of the carbohydrate fraction of the pulp occurring during the longer periods of digestion. Lewis and coworkers^{93,94} also concluded, when the lignin content of a pulp is greater than a certain maximum (which they found to be 8.6% lignin or less) that papers made from the pulp will be low in strength. However, at lignin contents below 8.6% (in alkaline-cooked pulps), they believe the lignin is located mainly in the secondary wall of the fiber where it interferes less with fiber bonding. The results, which were obtained using a spruce pulp made by the neutral sulfite process and then delignified by the kraft process, are shown in Figure VII-2.⁹⁴ Hall⁹⁵ found a maximum in tearing strength at a lignin content of about 5% for both sulfite and sulfate pulps, but found that burst and tensile strength decreased progressively with lignin contents lower than 7.1%, as shown in Table VI, for different sulfite pulps. Jayme and Wettstein⁹⁶ found that maximum strength was obtained at a lignin content between 4 to 6%. When the lignin was removed from asplund pulp by chlorination, Maass and de Montigny⁹⁷ obtained maximum bursting strength at 4%

⁹² J. M. Limerick and A. J. Corey, *Pulp Paper Mag. Canada* 47: 62-66, 84 (Mar., 1946)

⁹³ H. F. Lewis, F. E. Brauns and M. A. Buchanan, *Tech. Assoc. Papers* 22: 475-477 (June, 1939)

⁹⁴ H. F. Lewis and C. A. Richardson, *Paper Trade J.* 109, No. 14: 188-190 (Oct. 5, 1939)

⁹⁵ G. A. Hall, *World's Paper Trade Rev.* 91, No. 16: 1340-1354, 1396 (Apr. 19, 1929)

⁹⁶ G. Jayme and R. Wettstein, *Papier-Fabr.* 36, No. 49: 519-531 (Dec. 2, 1938)

⁹⁷ R. de Montigny and O. Maass, Canadian Dept. of Interior, *Forest Service Bull.* 82, (1935)

lignin in the case of spruce pulps. The above results, obtained for the most part on commercial pulps, indicate that there is an optimum lignin content for maximum strength, but, as pointed out in the preceding paragraph, the results are probably affected by a change in the other components of the pulp, in addition to the change in lignin content, brought about during pulping.

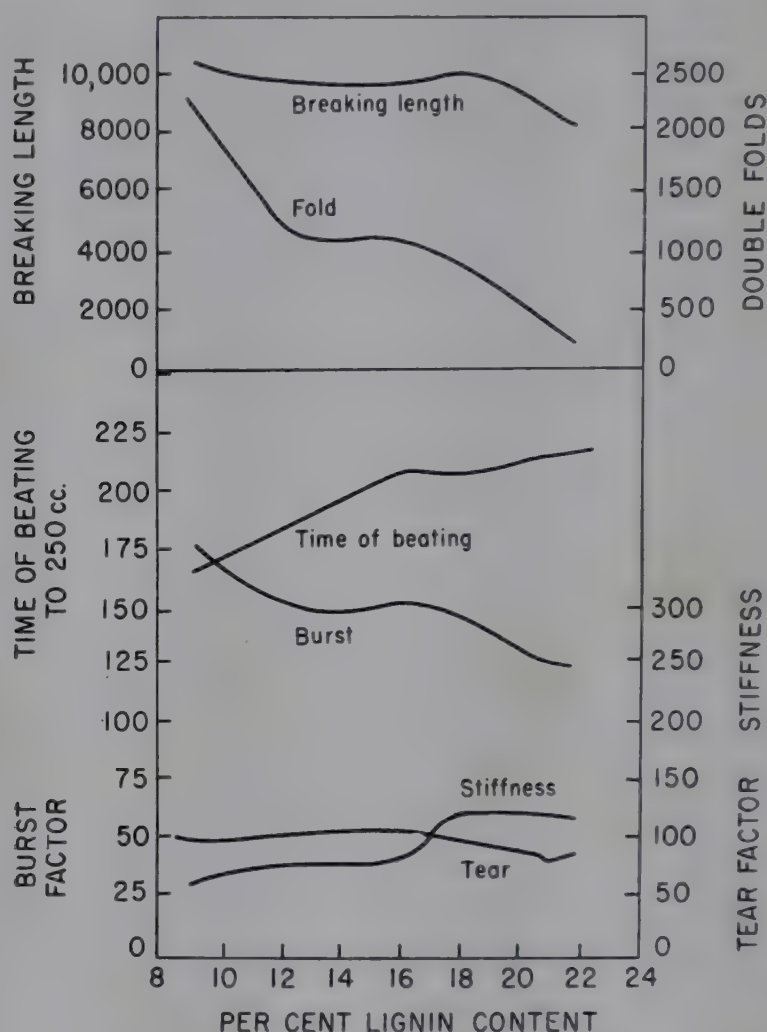


Fig. VII-2. Effect of lignin on strength properties of beaten pulp.

Using the Roe chlorine number as a measure of the amount of lignin and other oxidizable materials present, Genberg and Houghton⁹⁸ found that the bursting strength of unbleached sulfite increased practically linearly with an increase in Roe chlorine number over the range of 1.8 to 5.4 (permanganate number 10 to 23). Tearing strength also increased, but only up to a Roe number of 3.8, after which it declined sharply. Pascoe⁹⁹ found a definite correlation between bleach value and bursting and tearing strengths in the case of direct cooked sulfite pulps, but no correlation when forced circulation was used in cooking. His results showing the relation-

⁹⁸ G. P. Genberg and E. O. Houghton, *Paper Trade J.* 88, No. 17: 71-78 (Apr. 25, 1929); No. 18: 53-59 (May 2, 1929)

⁹⁹ T. A. Pascoe, *Tech. Assoc. Papers* 30: 422-426 (June, 1947)

TABLE VI

EFFECT OF LIGNIN CONTENT ON SHEET STRENGTH OF BEATEN SULFITE PULPS

Type of pulp	Lignin content, %	Bursting strength, %	Folding endurance, double fold	Tearing strength, g./16 strips	Breaking length, meters
Indirect cooked, strong unbleached sulfite pulp	7.1	172	2,806	43	10,380
Indirect cooked, strong unbleached sulfite pulp	5.7	165	2,562	44	9,860
Indirect cooked, strong unbleached sulfite pulp	4.9	152	2,480	48	9,360
Direct cooked, unbleached sulfite pulp	3.8	119	2,030	46	7,480
Bleached sulfite pulp		90	731	32	5,180

ship between bleach value (as measured by the permanganate number) and the burst value (sum of the burst tests at the 5- and 25-minute beating

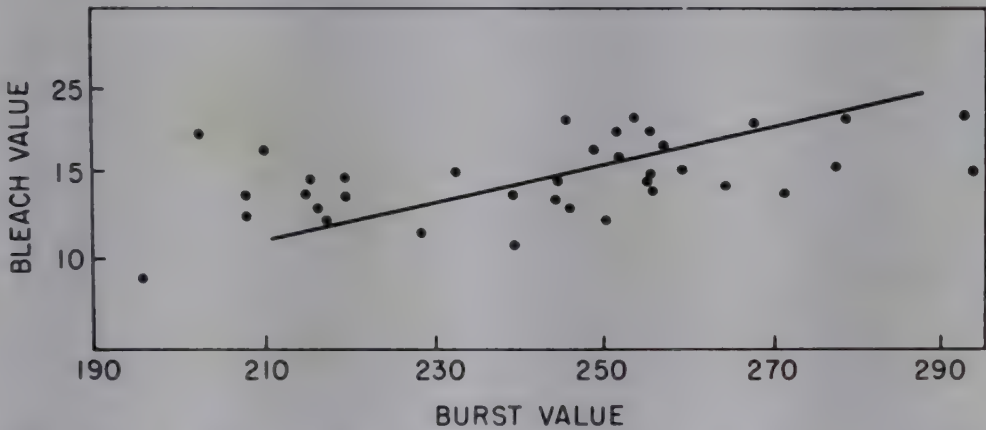


Fig. VII-3. Relationship between bursting strength and bleach value (permanganate number) of unbleached spruce sulfite.

periods expressed as a per cent) are shown in Figure VII-3 for unbleached spruce sulfite.¹⁰⁰ Statistical methods were used for drawing the curve.

Springwood and Summerwood Fibers

In the preceding chapter, it was pointed out that springwood and summerwood fibers are affected differently by the beating operation. This difference in beating properties can be attributed to a difference in the thickness of the fiber walls. For example, the walls of the summerwood fibers in some softwoods may occupy close to 100% of the total area, compared with only 30% for the springwood fibers. Because of their thin walls, springwood fibers tend to collapse on beating and, as a result, tend to produce a sheet of greater density than the thick-walled, stiff summerwood fibers.

¹⁰⁰ T. A. Pascoe and M. Fraser, *Paper Trade J.* 112, No. 12: 143-148 (Mar. 20, 1941)

Curran¹⁰¹ found that sheets containing the highest percentage of springwood fibers had the highest bursting strength, whereas the presence of summerwood fibers in a sheet tends to increase the tearing strength. One reason that birch pulp generally produces stronger papers than other hardwood pulps is the thinner walls of birch fibers.

Another virtue of springwood fibers is that they improve the uniformity and smoothness of the sheet, which is very important in the case of writing and printing papers. Sheets made from 100% springwood fibers have a dense, well-knit structure, whereas those made from 100% summerwood fibers are extremely coarse in texture. The photomicrographs in Figure VII-4 are of theoretical interest, since they illustrate the difference in texture between an all-springwood and all-summerwood sheet.¹⁰¹

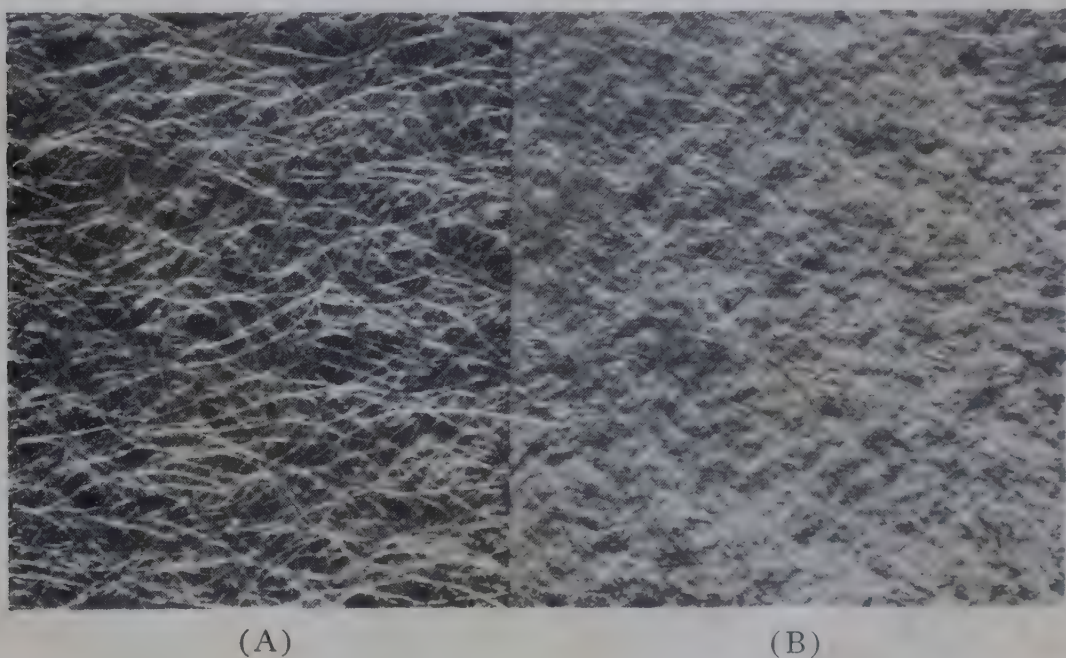


Fig. VII-4. Papers made from all summerwood fibers (A) and all springwood fibers (B). (Photograph from Forest Products Laboratory, U. S. Forest Service.)

Comparison of Different Pulps

Each commercial pulp produces a sheet of distinctive properties because of the differences in the fundamental characteristics of its component fibers. These differences make each pulp most suitable for a particular grade of paper. Although it would be impossible to describe the various properties of each of the commercial pulps, a few examples are mentioned below to show how each outstanding property is connected with a specific feature of the pulp.

Kraft pulps from the southern pines and from West Coast hemlock, both of which have exceptionally long fibers, produce papers of high tearing strength. Because of this property, these pulps are particularly well suited

¹⁰¹ C. E. Curran, *Paper Trade J.* 103, No. 11: 200-204 (Sept. 10, 1936)

to the manufacture of papers requiring high resistance to tear, such as bag papers. Douglas fir pulps produce sheets with very high tearing resistance (because of their long fiber length), but these sheets are bulky and porous and have low bursting strength.

Chestnut pulp makes an outstanding material for the corrugating medium in corrugated board because of its short, stiff fibers and high pentosan content, which imparts a high degree of stiffness to the board. Straw pulps are also suitable for corrugating media because of their high hemicellulosic content which tends to produce a stiff sheet.

Esparto pulps are especially useful for lightweight printing papers, where they produce an ideal combination of good formation, texture, and high opacity owing to the thin fibers which do not fibrillate easily. Soda (hardwood) pulps are also well suited for printing papers because of their short fiber length and poor "wetting" properties, which favor a sheet of high opacity and smooth surface (but low strength). Groundwood pulps are also used in printing papers, and in addition they make good insulating boards because of the rough, springy fiber bundles which contribute to low density and good insulating qualities, because of air spaces in the board.

True Manila hemp makes exceptionally strong, tough, and pliable papers because of its long fibers, which are readily fibrillated on beating; and hence, this pulp is used in the manufacture of unusually strong papers.

Cotton rag pulps make strong sheets because of their great fiber length and facility for fibrillation. They are particularly useful for permanent papers because of their high content of resistant cellulose. Sulfite (softwood) pulps are particularly useful for writing papers because of their rapid "wetting" properties and good strength.

The above list could be continued indefinitely, but the examples given illustrate how the useful properties of a pulp are tied in with some outstanding characteristic. Other examples are mentioned from time to time in other chapters.

Effect of Alumina, Sizing, Fillers, etc.

The addition of almost any substance to the fibrous furnish reduces fiber bonding. This is especially true for hydrophobic substances such as rosin or paraffin, which result in a very great decrease in strength, and it is also true to a lesser extent for some of the hydrophilic materials such as clay and alumina. The loss in strength which occurs when paper is sized with rosin is well recognized. This loss in strength is less for papers made from lightly beaten or unbeaten pulp than for papers made from well-beaten pulp and, in fact, rosin may actually increase the strength slightly if the pulp is unbeaten.¹⁰² Groundwood papers may also be increased somewhat

¹⁰² H. Ellern-Eichmann, *Papier-Fabr.* 31, No. 12: 197-201; No. 13: 209-213; No. 14: 222-226 (Mar., 1926, Apr. 2, 1933)

in strength by the use of rosin size, but ordinarily, most papers are reduced in strength. Too much kerosene or other antifoam added at the paper machine also reduces interfiber bonding.

A few substances increase the strength of the sheet when included in the fiber furnish. These belong to the class of high molecular weight, hydrophilic colloids of which starch, proteins, and vegetable gums are examples. These materials act by being adsorbed on the fiber surface where they hold the sheet together through a fiber-to-binder-to-fiber bond. The effect of these materials is discussed in a later section.

The effect of pH on beating and fiber bonding has been discussed in the preceding chapter. In addition to the apparent slight effect on the original strength, pH has a very great effect on the permanence of the paper. Alum has a very decided effect on sheet strength, since it reacts with alkali in the water to form alumina floc, which has a harmful effect on fiber bonding. The effect of alumina on the strength properties of paper has been studied by Keller, Simmonds, and Baird,¹⁰³ who showed that alum reacts with bicarbonates and hydroxides occurring in natural waters to form sufficient alumina floc to lower appreciably the strength of the paper, particularly the bursting strength. Poorly washed alkaline-cooked pulps contain enough residual alkali to increase greatly the alum demand, thereby producing an excessive amount of alumina floc and lowering the strength. Chesley and coworkers¹⁰⁴ found that as much as 20 to 28 lb. of alum per ton of pulp may be required in addition to the normal amount to bring a poorly washed sulfate pulp to a pH between 4.5 and 5.0.

The effect of pigments on sheet strength is discussed in Chapter IX, and the effect of rosin size is discussed further in Chapter X.

Bonding between Plys of Multi-Ply Board

The degree of bonding which takes place between the plys of multi-ply board made on a cylinder machine is important in determining the over-all strength of the board. On cylinder machines, the stock carried in the vats for the outside plys of the board is ordinarily quite different from the stock carried in the vats for the filler plys. This process, called vat lining, poses the problem of bonding fibrous stocks of different nature.

Brown¹⁰⁵ found that the factors involved in the bonding between the plys of multi-ply board are much the same as those involved in interfiber bonding in a sheet of paper. These have already been discussed, but it should be pointed out that the amount of beating given the stock is the most

¹⁰³ E. L. Keller, F. A. Simmonds and P. K. Baird, *Paper Trade J.* 112, No. 1: 8-12 (Jan. 2, 1941)

¹⁰⁴ E. H. Smith, A. B. Moore and K. G. Chesley, *Paper Trade J.* 112, No. 20: 239-241 (May 15, 1941)

¹⁰⁵ D. A. Brown, *Paper Trade J.* 112, No. 3: 27-28 (Jan. 16, 1941)

important single factor because of its effect in increasing the "wetting" and fibrillation, and hence the area of contact between the plys.

Increased beating results in a gain in the over-all strength of multi-ply board just as it does for homogeneous sheets. There is, however, a complication in the case of multi-ply boards, since the amount of beating given to the stock in adjacent plys cannot be widely different, although in general no trouble will be experienced if the freeness of the stock in adjacent plys does not differ by more than 125 cc., as measured on the Canadian standard freeness tester. Another important factor is the amount of water carried at the interface between plys, since the greater the amount of water in the sheet at this point, the greater the freedom of movement of the fibers and the more continuous the network which is produced. Wet pressing increases bonding. However, calendering tends to decrease bonding, and too rapid drying may also decrease bonding by forming steam pockets between the plys.

Some mills have experimented with the spraying of cementing substances between the plys. Among the substances used for this purpose are resins, starches, and starch-resin combinations. The object is to add greater strength to the board and to increase its stiffness, but so far, these attempts have not been very successful. However, the addition of starch to the stock at the beaters is beneficial in increasing the amount of bonding between plys. In a practical mill test, the addition of 4% cooked oxidized starch to the liner stock of patent coated board resulted in an increase in Dennison wax test from a number 14 wax to a number 18 wax, due to increased bonding between the liner and filler plys of the board. There is a special grade of cylinder board (known as K-B board) which contains a layer of asphalt between two of the plys. In making this board, asphalt emulsion is applied by means of a special roller to the partly formed sheet between two of the cylinders. The addition of asphalt in this way increases the moisture resistance of the board.

As can be seen from the above, the problems in obtaining a good bond between plys of dissimilar stocks in multi-ply board are more difficult than the problems involved in interfiber bonding in homogeneous sheets. This explains why multi-ply paperboard is never as strong as a board of the same thickness made in the form of a homogeneous sheet on a Fourdrinier machine. For this reason, Fourdrinier or single-ply boards are better suited than multi-ply boards for those uses where there is danger of the paper splitting, as, for example, in boards which are used for saturation with asphalt. There are, however, many purposes for which multi-ply boards are admirably suited, and some of the combinations which are made commercially are described below.

Chipboard. Chipboard is a grade of cylinder machine board which generally contains the same stock in all plys, always waste paper stock. This board is made in a wide range of thicknesses. Both "bending" and "non-bending" grades are made.

Mill and Bogus Bristols. Mill bristols, which are called by this name to distinguish them from index bristols made on a Fourdrinier machine, are used mostly for show cards and advertising. Bogus bristols are used for cheap cards and tickets. They are generally made from waste papers, blank or over-issue news, or waste kraft.

Folding Boxboards. If bending qualities are necessary, as in the case of folding boxboards, the two outside plys of the board must be made from long-fibered stock such as bleached sulfite or bleached sulfate. This stock must be beaten moderately in order to develop the necessary folding endurance and reduce the amount of fuzz on the sheet, but jordaning of the liner stock is kept to a minimum in order to preserve the bending qualities. In comparison, the filler stock, which is usually derived from waste papers, is customarily jordaned quite heavily in order to eliminate lumps of undefibered stock or extraneous matter which may have been passed by the breaker beater.

Combination Manila Board. Another grade, known as combination manila board, is composed of filler stock consisting of a mixed furnish of unbleached sulfite and groundwood and liner stock, which is usually made from bleached sulfite and white shavings.

Patent Coated Board. Another highly important grade is known as patent coated board, which is an uncoated board used in the manufacture of printed folding boxes. It consists of a top liner made from strong, white stock to which must be imparted a good printing surface, good bending qualities, and good color.

Container Board. Still another grade is known as container board. In this board, the filler is made from mixed waste papers, and the liner is generally made from kraft fiber, which may be all virgin kraft or a mixture of virgin kraft and waste kraft. If waste kraft is used, the board is sometimes referred to as jute liner board. Jute liner board may be given either a dry finish or a water finish, and in some cases the board is calender-sized with starch, carboxymethylcellulose, etc. Filled kraft liner board is similar to jute liner board except that virgin kraft stock is used in the liners. These grades are made in the standard thicknesses of 12, 16, or 30 points.

Set-up Boxboard. Set-up boxboards differ from bending boxboards in that bending quality is not required. As a result, this grade is usually made of short-fibered stocks such as groundwood, news, straw, or mixed papers. In some cases, the liners may be made from bleached white stock in order to improve the appearance.

Other Grades of Board. Other grades of cylinder machine board include laundry board, calendar board (usually a white patent coated board or a clay-coated board), cracker caddies (usually a jute-lined board), bottle-cap board (usually lined with sulfite stock), and match book board (either a bleached manila-lined board or a white patent coated board). In the case of milk bottle-cap board, it is desirable to have a weak bond between two of the plys so that a tab can be readily raised on the cap when removing the cap from the bottle. Weakening of the bond can be achieved by adding wax emulsion to one of the plys at the point where the split is to occur.

Duplex Paper. Duplex paper is a special grade of two-ply paper which is made on either a two-cylinder machine or on a combination cylinder and Fourdrinier machine. The product is used for bag papers, for example, duplex flour sacks, which have a white ply on the outside and a dark blue ply on the inside. In the past, the blue ply was made from 100% rope and the outside ply from part rope stock and part sulfite pulp. Since it was customary to beat the rope stock for the inside ply to a lower freeness than the stock for the outside ply, considerable trouble was often experienced in obtaining a good bond between the plys. It was therefore necessary to have the plys very wet at their point of contact and to use graduated pressure on the wet presses in order to reduce the danger of crushing.

Backliners. On all the above grades of board, it is possible to use a backliner of different stock between the filler and the top liner. This backliner helps to improve the cleanliness, brightness, and formation of the board, and hence is effective in improving the printing surface. The object is to cover up the dark filler stock and produce a better foundation for the liner stock. News stock is a common grade for use as a backliner, and a board made in this manner is said to have a "skim news backing."

Use of Hydrophilic Binders

Pulp fibers contain natural hydrophilic substances in the pentosans and other hemicellulosic materials which act as cementing agents in inter-fiber bonding. These substances are not true binders in the ordinary sense of the word, since their potential adhesiveness is not developed until the pulp is beaten. Moreover, many pulps are either deficient in these natural bonding agents or the pulp is not beaten long enough to take full advantage of them, so that it is desirable to add additional binder to the pulp prior to sheet formation. There are many materials which can be used to increase fiber bonding, but many of them are either too expensive or too inefficient to be important commercially. Some of the materials used commercially are discussed below.

Functions of Binders

Although each hydrophilic binder acts in a different manner, the principal function of these materials, when added to the beater, is to increase the strength of the paper. Other important functions are to lay surface fuzz, increase the hardness and durability, increase the stiffness and rattle, and with some colloids, to improve the sizing. Because these materials tend to increase strength, their use makes it possible to carry a higher percentage of filler in the paper, if desired. Rowland¹⁰⁶ points out that if improved binders could be found they would permit the production of papers with higher porosity, better formation, and higher strength than is now possible. Such papers would also possess, in addition to their other good properties, a higher opacity, better compressibility during printing, increased dimensional stability, and reduced curl and cockle during humidity changes.

Amount of Binder Used

The total amount of cementing substance which is necessary in pulp fibers to form a strong sheet of paper is quite high. Clark¹⁰⁷ has shown that it requires at least 18% of added gum to form a sheet of appreciable strength, using artificial (rayon) fibers which contain no natural binder. His results¹⁰⁸ showed that the bursting and tensile strengths increase approximately linearly with the logarithm of the amount of mucilage, i.e., vegetable gum, added to the paper under these conditions. However, there is an optimum amount of binder and cementing material beyond which additional amounts do little or no good. For example, it has already been pointed out that there is an optimum hemicellulose content for pulp, and it can also be shown that there is an optimum point beyond which the further addition of colloidal substances, such as starch, does little or no good. In general, maximum strength is realized when there is sufficient adhesive to produce a more or less continuous film around the fibers. Additional adhesive beyond this point merely increases the thickness of the adhesive film (and hence its brittleness) without proportionally increasing the bursting and tensile strengths of the paper.

Use of Proteins

Animal glue is not so widely used as some other binders, but it may be added to the beater to increase the retention of fillers, to improve sizing, to improve hard water conditions, or to lay surface fibers.¹⁰⁹ In general, other proteins such as casein and soy protein are not widely used for increasing

¹⁰⁶ B. W. Rowland, *Paper Ind.* 27, No. 9: 1398-1404 (Dec., 1945)

¹⁰⁷ J. d'A. Clark, *Paper Trade J.* 115, No. 26: 328-334 (Dec. 24, 1942)

¹⁰⁸ J. d'A. Clark, *Pulp and Paper Mag. Canada* 44, No. 1: 92-102, Convention Issue (1943)

¹⁰⁹ H. B. Sweatt, *Paper Ind.* 27, No. 5: 711-718 (Aug., 1945)

the strength, although they are used in combination with rosin size in certain sizing processes. Soy flour is not very effective, although fairly good results are obtained when it is used in asbestos papers. A special glue, called Sveen glue, is sometimes used to improve formation and increase the retention of fillers, dyestuffs, etc. (see Ch. VIII).

Use of Water-Soluble Cellulose Derivatives

Water-soluble cellulose derivatives are sometimes used for improving fiber bonding. Methylcellulose has been found to improve sheet strength.^{110,111} Musser and Engel¹¹² found, on the basis of laboratory experiments, that water-soluble methylcellulose had no significant effect when added to beaten stock, but that it greatly increased the burst, tear, and breaking length when added at the beginning of the beating period. The high-viscosity types are most effective. Methylcellulose tends to lower sizing when used in small percentages, although there is some beneficial effect at higher percentages. The retention of methylcellulose appears to be about 30 to 40%, based on methoxyl determinations.¹¹² Foaming is somewhat of a problem.

Horsey,¹¹³ using sodium carboxymethylcellulose which was precipitated by alum in the beater, obtained an increase in strength and sizing in stocks of high freeness and a decrease in porosity and opacity when used in stocks of intermediate to low freeness. Edge¹¹⁰ also reported increased sheet strength from carboxymethylcellulose. Carboxymethylcellulose is being used commercially in paperboard, particularly jute liner, to the extent of 1 to 2 lb. per ton to obtain bursting strength improvement of about 10%.

Use of Vegetable Gums

Vegetable gums such as locust bean gum and guar are highly interesting materials from the standpoint of increasing fiber bonding. These gums also tend to improve formation through their dispersing effect on the fibers and are sometimes added for that purpose (see Ch. VIII).

Locust bean gum is reported¹¹⁴ to bring about a significant improvement in bursting strength, tensile strength, and fold endurance when beaten along with the fiber furnish. Addition of gum to the beaten stock did not

¹¹⁰ S. R. H. Edge, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 77: 189 (June, 1946)

¹¹¹ R. E. Collins, "The Effect of Beater Additives on the Physical Properties of Sulfite Pulp," unpublished thesis, New York State College of Forestry, Syracuse, N. Y. (1948)

¹¹² D. M. Musser and H. C. Engel, *Paper Trade J.* 115, No. 8: 85-87 (Aug. 20, 1942)

¹¹³ E. F. Horsey, *Paper Trade J.* 125, No. 4: 40-44 (July 24, 1947)

¹¹⁴ J. E. Jayne, J. C. Tongren and D. T. Jackson, *Tappi* 33, No. 1: 32-35 (Jan., 1950)

produce much strength improvement. No appreciable strength increase was obtained on hardwood pulps.

Guar is a new product which promises to find use as a beater size and, in fact, has been produced and sold for this purpose, although later production was discontinued. When added dry at the beater, guar acts as a strong cementing agent which greatly increases the strength of the paper, even when only small percentages are added. Rowland¹¹⁵ found guar to be several times as effective as an equal amount of starch, especially in kraft papers. The amount of guar required to produce a great increase in the dry strength of the paper is normally quite small. For example, with from 0.25 to 1.0% guar based on the weight of the fiber, it is possible to obtain marked increases in burst and tensile strength; or, by reducing the amount of mechanical treatment, it is possible to hold the burst the same and greatly increase the rate of drainage on the machine. If sheets containing guar are treated with borax, they develop a degree of temporary wet strength. Rowland reports that excessive iron in the water or in the pulp has an adverse effect on guar added at the beater.

Use of Wet-Strength Resins

Another class of fiber bonding material is that typified by the urea or melamine formaldehyde condensates or wet-strength resins. These are used for increasing the wet strength of paper, but they have the incidental effect of increasing dry bonding. On a mixture of sulfite and soda pulps for offset papers, it was found¹¹⁶ that 2 to 3% of melamine formaldehyde resin and one and a half hours' beating produced papers with equal or superior bursting strength to that obtained with no resin and nine or more hours of beating. In addition, the sheets containing resin showed less expansion and less tendency to curl. Since the bonds which are produced by these resins are of an entirely different nature from those produced by other hydrophilic materials, their effect has been discussed in a separate chapter (Ch. XII).

Use of Sodium Silicate

Sodium silicate has been used as a regular part of the furnish of a number of different grades of paper for many years. Its effect is, however, somewhat different from the hydrophilic binders described in the preceding section. Among the effects which may be produced by sodium silicate when added to the beater are: increased stiffness and rattle, improved finish, reduced amount of surface fuzz, increased retention of fillers and fiber fines, increased ash, and a slightly increased bursting strength.

¹¹⁵ B. W. Rowland, *Paper Ind.* 27, No. 9: 1398-1404 (Dec., 1945)

¹¹⁶ C. G. Weber, M. B. Shaw, M. J. O'Leary and J. K. Missimer, *Paper Ind.* 30, No. 1: 83-88 (Apr., 1948)

Because of its alkaline nature, silicate increases the rate of "hydration" of the pulp. Generally speaking, most alkalies will increase the beating rate, but the effect of silicate is somewhat greater than equivalent amounts of other alkalies, due perhaps to greater adsorption on the fibers. A saving of 5 to 10% in power is often attained. For most purposes, about 2 to 4% silicate is used, and this may be expected to increase the burst test by about 10% and to add about 1% to the ash of the paper.

For best results, silicate should be added early in the beating cycle, although if dyestuffs are present which are affected by high alkalinity, this may not be practical. After the silicate is thoroughly mixed with the stock, alum is added and allowed to react for a period of time. The pH should be brought to approximately 4.5 in order to obtain the maximum amount of precipitate, although the pH can subsequently be raised to about 6.5 if desired.

The nature of the precipitate formed with silicate and alum is unknown, though it is mostly aluminum hydroxide and hydrated silicic acid, with some aluminum silicate present. In addition, the floc tends to carry some sodium out of solution, probably in an adsorbed condition. Retention averages about 60%.

As a general rule, silicates which are high in silica ($\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ or $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$) are preferred, since they are most effective and require less alum than low-ratio silicates. For 100 lb. of $\text{Na}_2\text{O} \cdot 3.86 \text{ SiO}_2$, approximately 25 lb. alum is required; for $\text{Na}_2\text{O} \cdot 3.3 \text{ SiO}_2$, approximately 33 lb. is required.¹¹⁷

Use of Starch

Among the many uses of starch in the paper industry is its use in the beater. The principal function of starch when applied at the beater or similar location is to increase the strength of the sheet and reduce surface fuzz. This process is generally referred to as beater sizing with starch, although the process is not a sizing process at all in the usual sense of the word, since the water and ink resistance of the paper are ordinarily not affected. With one special type of modified starch, namely the oxidized starches, the sizing is generally improved, but this is due to the beneficial effect which this type of starch has on the precipitation of the rosin size and is not due to the starch itself. Therefore, it should be borne in mind that the term "sizing" when applied to starch usage in the beater refers to improvement in fiber bonding.

The adhesive qualities of starch for papermaking are due to its content of polar hydroxyl groups. These groups have a mutual attraction for the hydroxyl groups in the pulp fiber, and set up a fiber-to-starch-to-fiber

¹¹⁷ J. G. Vail, *Soluble Silicates in Industry*, The Chemical Catalogue Company, New York (1928)

bonding, which may be stronger than fiber-to-fiber bonding, and, as a result, the strength of the sheet is increased. Of the two fractions in ordinary starch, the amylopectin is the one which is more important, the amylose fraction having poor bonding qualities due to its pronounced tendency to retrograde.

Use of Uncooked or Partially Cooked Starches. In some cases starches are added to the beater without being cooked. This procedure is satisfactory only if the temperature of the paper machine driers is high enough to gelatinize the starch granules in the wet sheet. Otherwise, no value is derived from the uncooked starch granules, which then act as a filler and lower the strength of the paper. To gelatinize the uncooked starch granules in the sheet, enough heat must be available to raise the temperature of the wet sheet to between 165 and 195° F. during the first few minutes of drying while there is still enough water present to gelatinize the starch.

Tapioca starch has a lower gelatinization temperature than corn starch, and for this reason sometimes works better than corn starch when added uncooked to the fiber furnish. However, if there is sufficient heat on the driers, all native or unmodified starches, including corn and tapioca, act in about the same manner. Under these conditions, the starch granules are greatly swollen by the heat, and part of the starch is solubilized. This soluble starch tends to adhere to the surfaces of the fibers, but the remainder of the starch exists in the form of swollen starch granules which are distributed rather unevenly throughout the sheet. If the sheet is stained with iodine and examined under the microscope, the swollen granules are readily visible, since they stain reddish purple with iodine, whereas the adsorbed soluble starch, which is mostly amylose, causes the fiber to stain a blue color. Hypochloride-oxidized corn starch is quite effective as a beater starch when used uncooked, since it has a lower gelatinization temperature than the native corn starch, which permits easier "pasting" in the sheet. Furthermore, its reduced viscosity and greater dispersibility permits better distribution throughout the sheet after the starch has been gelatinized by the heat of the driers.

Because native starches are not very effective when added to the furnish uncooked, they are often partially cooked before being added. For example, it is common practice in some paper mills to heat native corn starch to the point where the granules just start to swell (about 170° F.) before adding to the beater. Under these circumstances, less heat is required to complete the pasting of the starch in the sheet on the driers.

Use of Cooked Starches. In cases where thoroughly cooked starch is used, the starch is first slurried in cold water and then heated to a temperature between 185 and 212° F. and held there for at least fifteen to thirty minutes. This results in a completely cooked starch solution which

can be added directly to the beater. On some grades of papers, sodium hydroxide is used in place of heat to gelatinize the starch. In this method, the starch slurry is prepared in the same manner, but enough alkali is added to cause gelatinization without the use of heat. This process is sometimes used in the preparation of starch for asbestos papers and papers made from southern kraft or Douglas fir pulps. The effect of the amount of heating of the starch on the bursting strength of the sheet is shown in Figure VII-5. In carrying out these laboratory tests, the starch suspension was heated to various temperatures before adding to the stock. It can be seen from the curve that heating to 185 to 200° F. is necessary in order to obtain the full effectiveness of the starch. These sheets were air-dried in order to prevent any further pasting of the starch while the sheet was being dried.

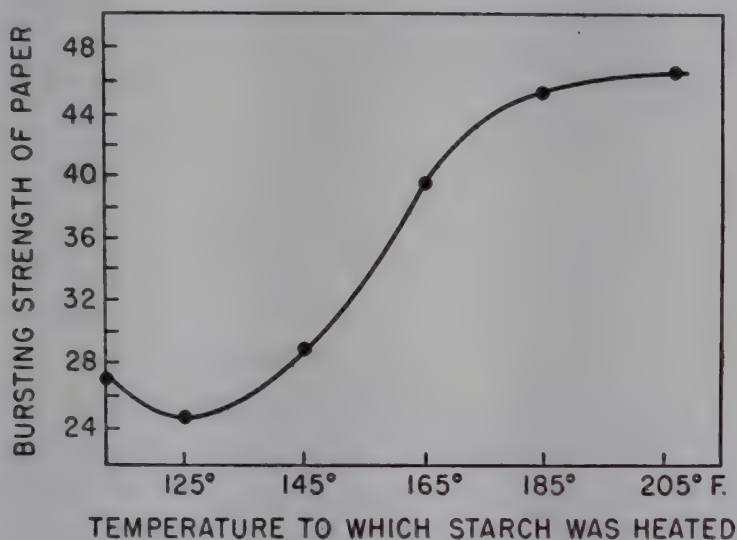


Fig. VII-5. Relation of temperature of heating to the effectiveness of starch solution added at the beater.

Use of Pregelatinized Starch. Pregelatinized starches are sometimes used in beater sizing. These starches have been treated so that they form a viscous paste in cold water without the necessity of heating. Consequently they can be added dry to the beater. However, most of these products do not redisperse well in the stock because of the retrogradation which occurs when the starch is cooked and dried during manufacture. As a result, these products tend to form "shiners" in the paper. Pregelatinized potato starch works better than corn because of its lower tendency toward retrogradation, and Kerr¹¹⁸ has described a method of treating corn starch so that it will retrograde less and hence redisperse more readily in the beater.

Special starches which have been treated so that the granules are partially ruptured and will gelatinize at a relatively low temperature have been

¹¹⁸ R. W. Kerr, U. S. 2,108,862 (Feb. 22, 1938)

tried as a beater starch. These starches function on the same principle as partially cooked starches.

Dispersibility of Cooked Starch. Considerable variability in results have been experienced in the use of beater starch in the paper industry. This has even led, in some quarters, to the opinion that starch has very little value as a beater sizing agent, but it is now generally realized that starch can be employed with excellent results if the proper starch is used under the right conditions. The type of starch which gives best results is determined by the structure of the sheet in which it is used. In other words, the results are affected both by the degree of physical dispersion of the starch and the density of the paper in which the starch is used.¹¹⁹

On the basis of numerous laboratory and practical mill tests, the conclusion has been reached that highly dispersed starch solutions are more effective than poorly dispersed starch solutions when used in high-density papers. Highly dispersed solutions are most effective in this type of paper because of the large number of colloidal starch particles which permit the formation of a greater number of fiber-to-starch-to-fiber bonds. Oxidized starches are very effective in high-density sheets because they form highly dispersed colloidal solutions, but on the other hand, poorly dispersed starch solutions, such as those obtained by cooking native corn starch, are quite ineffective in high-density sheets. Solutions of native starch contain only about 50% of the starch in the form of a colloidal solution, with the rest in the form of relatively large swollen granules about 20 microns in diameter. Consequently, there is correspondingly less starch available for fiber bonding, since the swollen granules offer only a small amount of external surface.

When low-density sheets are considered, the situation is reversed. Here the suspension of large swollen granules (found in native starch dispersions) is more effective than the colloidal solution (produced by oxidized starches), because the large granules help to form "bridges" between the fibers. Some chemists refer to this phenomenon as "spot welding" of the fibers at their points of intersection. To help visualize these situations, a diagrammatic sketch is shown in Figure VII-6, illustrating the conditions which prevail when both a colloiddally dispersed starch and a coarsely dispersed starch are used in a high- and a low-density sheet. As can be seen, the highly dispersed starch is wasted in the low-density sheet because it does not contact two or more fibers at many points. In contrast, the larger granules in the poorly dispersed starch suspension are more effective in the low-density sheet because of their larger size, which causes them to "bridge" fibers. On the other hand, the highly dispersed starch is very effective in the high-density sheet where there is considerable fiber-to-fiber contact,

¹¹⁹ J. P. Casey, *Paper Ind.* 26, No. 10: 1277-1280 (Jan., 1945)

whereas coarsely dispersed granules are relatively ineffective because the granules do not cover enough surface.

The above observations have been verified in many instances. Coarse papers of low density, e.g., roofing felts and papers made from southern kraft or Douglas fir pulps, show the greatest improvement in strength when treated with a cooked suspension of native corn starch, because of the presence of large swollen granules in the suspension. On the other hand, high-

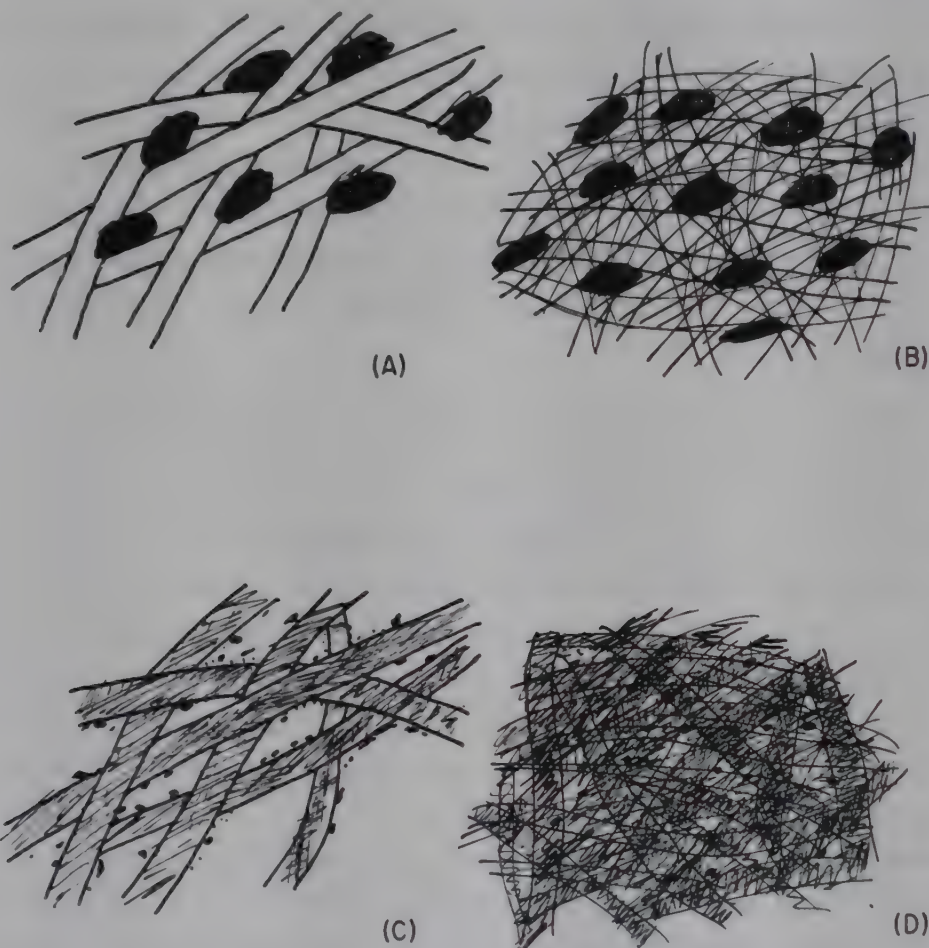


Fig. VII-6. Effect of highly dispersed starch and poorly dispersed starch in high- and low-density papers: (A) poorly dispersed starch, low-density paper; (B) poorly dispersed starch, high-density paper; (C) highly dispersed starch, low-density paper; (D) highly dispersed starch, high-density paper.

grade papers such as bonds and writings, which have a higher density, are more effectively treated with colloidal solutions, such as those obtained from the oxidized starches. In fact, most grades of commercial papers are high enough in density that the highly dispersed starches are most effective. Houtz¹²⁰ has pointed out the desirability of adding starch in the state of optimum colloidal dispersion, but neglected to observe that this is true only for high-density papers.

¹²⁰ H. H. Houtz, *Paper Trade J.* 113, No. 6: 66-70 (Aug. 7, 1941)

Types of Starch Used in Beater Sizing. Several types of starch are used commercially in beater sizing. These include both the native starches and the modified starches. The effects which are obtained depend upon the grade of paper in which the starch is used and also upon the degree and type of chemical modification. One general rule is that a high-viscosity starch of high intrinsic strength will produce greater strength than a low-viscosity starch. This has been recognized in a general way by most papermakers, and Houtz¹²⁰ verified it by showing that there is a definite correlation between the molecular weight of the starch and the increase in strength which is obtained from it. However, in order for this relationship to be valid, the starch must be thoroughly cooked and dispersed. Cobb and coworkers¹²¹ are not convinced of the value of native starch in commercial papers, inasmuch as they believe that high-viscosity starches lower the freeness unduly and induce an excessive contraction of the sheet on drying; and for this reason, they favor the use of modified starches of low viscosity.

Oxidized starches are used in the beater because they produce better results than other types of starch on certain grades of paper. As just mentioned, they are particularly efficacious on high-density sheets. Moreover, they have the unique property of improving the results with rosin size by causing the size to be precipitated by alum in a more effective form. As a result, marked increases in the water and ink resistance of rosin-sized sheets can be obtained by the use of 2 to 5% hypochlorite-oxidized starch on the weight of the pulp. It is possible in commercial tests to increase the sizing value by as much as 25 to 50% through the use of this amount of oxidized starch.

Amount of Starch Used. The proper amount of starch to use is a controversial point among papermakers. This is not surprising, since there are so many different factors which affect the results. Cobb¹²² believes that maximum strength is obtained at about 0.5% starch on the basis of the pulp when the starch is not excessively degraded. Theoretically, it should require very little starch to completely cover the surface of the fibers if the starch is well dispersed and adsorbed by the fiber. However, practical experience has been that up to 5 to 7% starch, and even higher, on the basis of the pulp, can be used with beneficial results, although normally between 2 to 3% starch is the most economical.

In general, the maximum amount of starch which can be used with profit is greater for the modified starches, such as the oxidized starches, than it is for the native starches. Figure VII-7 illustrates the effect ob-

¹²¹ R. M. Cobb, D. V. Lowe, E. Pohl and W. Weiss, *Paper Trade J.* 105, No. 7: 105-108 (Aug. 12, 1937)

¹²² R. M. Cobb, D. V. Lowe, E. Pohl and W. Weiss, *Paper Trade J.* 105, No. 7: 105-108 (Aug. 12, 1937)

tained on bursting strength in the laboratory when different percentages of oxidized and unmodified corn starch are added to the stock, with all starches being thoroughly cooked before addition. These results illustrate that native (pearl) starch is more effective when 1 to 1½% starch is used, while the oxidized starch is more effective when 2% or more starch is used. Many mills use up to 5 or 7% oxidized corn starch with excellent results. When such large quantities of well-dispersed starch are used, the fiber-to-fiber bonding probably becomes of lesser importance than the fiber-to-starch-to-fiber bonding.

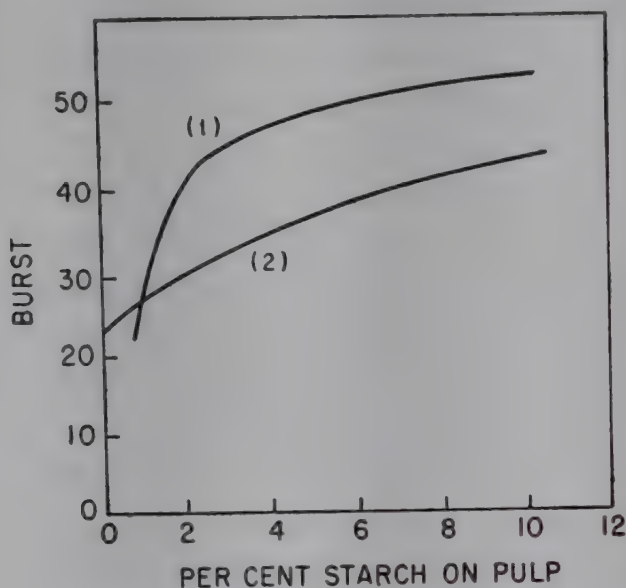


Fig. VII-7. Effect of oxidized starch (1) and unmodified (Pearl) starch (2) on bursting strength when added at the beater.

Distribution of Starch in Paper. Some paper chemists consider starch as being colloiddally adsorbed in the form of micelles on the fiber surface, but this is in all probability an idealized condition which is not often attained in commercial practice. For one thing, starch is not readily adsorbed on cellulose fibers, because the two have a like electrostatic charge and tend to repel each other. It is now believed that the amylose fraction of starch is readily adsorbed,^{123, 124} but that the amylopectin is adsorbed very poorly. Since amylopectin is the starch fraction which is primarily responsible for the bonding between fibers, the high adsorption of amylose means little or nothing, so far as sheet strength is concerned.

With most starches used in beater sizing, part of the starch is solubilized and part remains in granule form. These two fractions function differently in the sheet. The soluble starch tends to rise to the surface of the sheet opposite to the side in contact with the drier, whereas the residual granules remain in the interior of the sheet. These effects can be illus-

¹²³ C. Tauret, *Compt. rend.* 158: 1353 (1914)

¹²⁴ E. Pascu and J. W. Muller, *J. Am. Chem. Soc.* 63: 1168 (1941)

trated in the laboratory by drying test sheets containing raw native starch in contact with a drier without turning. If the sheet is then stained with iodine and examined by means of a microscope, it will be seen that the soluble part of the starch has migrated to the surface of the sheet, whereas the other part has remained in the interior of the sheet in the form of large swollen granules. Lee¹²⁵ has noted this effect and has published photographs showing the difference between the starch in the interior and on the top surface of tag paper when uncooked starch was added to the beater. It is quite possible to add starch at the beater and have most of it appear on the surface of the sheet, thus simulating a surface-sized effect.

The presence of starch in paper can be determined by either qualitative or quantitative procedures. A microscopic examination of the paper, after staining with iodine solution, is helpful in showing the distribution and degree of dispersion of the starch in the paper.

Retention of Starch. Because of its low affinity for cellulose, the retention of cooked starch in unsized sheets is usually quite low, most investigators reporting retention figures in the neighborhood of 10 to 50%. Beating by itself does not improve the retention of starch unless alum has been added to the stock.¹²⁶ Kress and Bialkowsky¹²⁷ found that the retention of starch is less than 10% on pure fibers (beaten or unbeaten).

Rowland¹²⁸ emphasizes the importance of alumina in improving the retention of starch. He found that alum is not effective in increasing starch retention in soft water, but if alum is used in hard water, a colloidal alumina floc is formed which is quite effective.¹²⁹ Sodium resinate size accomplishes the same purpose by hydrolyzing to form alkali, which in turn reacts with alum to form alumina. These examples readily demonstrate a fact which has been recognized in a general way for many years, namely, that the effectiveness of starch in beater sizing depends upon the presence of alumina. Rowland¹³⁰ and others¹³¹ suggest the use of additional alkali and alum over that normally used in order to obtain maximum starch retention. They believe that the alumina formed by the normal amount of sodium resinate and alum is inadequate for complete adsorption of the starch. Inasmuch as starch competes with fillers, rosin, certain dyestuffs, and similar substances for the alumina which is present, it is quite possible in any single furnish that there will be insufficient alumina to take care of the demand.

¹²⁵ H. N. Lee, *Paper Trade J.* 107, No. 6: 53-59 (Aug. 11, 1938)

¹²⁶ O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 219-228 (Nov. 12, 1931)

¹²⁷ O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 219-228 (Nov. 12, 1931)

¹²⁸ B. W. Rowland, U. S. 2,207,555 (July 9, 1940)

¹²⁹ B. W. Rowland, *Paper Trade J.* 97, No. 21: 249-250 (Nov. 23, 1933)

¹³⁰ B. W. Rowland, U. S. 2,207,555 (July 9, 1940)

¹³¹ D. K. Pattilloch and I. Pattilloch, U. S. 2,036,882 (Apr. 7, 1936)

On the other hand, it is possible to have too much alumina, and Rowland¹³² reports a condition where excessive quantities of hydrous alumina caused the starch gel to be so fully occupied that it was no longer available for bonding the fibers. Alumina beyond that required by the starch is undesirable in that it lowers the strength of the paper.

Rowland¹³³ believes that the starch-alumina complex exists as a delicate gelatinous body which is mostly attached to the fiber. Because of its delicate nature, mechanical agitation serves to dislodge it from the fiber.¹³⁴ Hence, when cooked starch is used, it is best to add the starch after the beating and jordaning. Many mills add their starch at the fan pump.

Other substances besides alumina may be used to increase the retention of starch. Kesler and Black¹³⁵ propose treating starch with fatty acid or soap and then precipitating a soap-starch complex on the fibers by the addition of metallic ions, e.g., aluminum. They claim improved retention and less "slowing" of the wet sheet on the wire. However, in the past too much emphasis has been placed on the retention of starch. Starch is like rosin in that retention in itself is no indication of the effectiveness of the starch in the sheet. Improperly prepared starch may show little benefit, even though its retention may be high, whereas a starch which is properly prepared may show exceptionally good results in spite of its low retention.

Grades of Paper Using Binders

The type and amount of binder which can be used economically depends on the grade of paper being made. In general, hydrophilic binders seem to give the greatest percentage gain in strength on rag papers and a proportionately lower increase in strength on chemical wood pulps or groundwood, with groundwood furnishes showing the poorest results. Some of the grades of paper which are customarily made with the help of hydrophilic binders are listed below:

Bond papers. These often contain from 2 to 4% of beater starch, in addition to a surface treatment with starch.

Bristols. These must be very stiff, and hence are usually made with 2 to 10% beater starch and 1 to 4% sodium silicate added at the beater.

Envelope papers. These usually contain about 3% beater starch.

Paperboards. Many grades of board are made with from 2 to 4% beater starch.

Kraft papers are ordinarily made without binders, although some vegetable gum is used in making these grades.

It should be pointed out that nearly all water-soluble colloids show much greater improvements in sheet properties when tested in the labora-

¹³² B. W. Rowland, *Paper Trade J.* 111, No. 9: 101-104 (Aug. 29, 1940)

¹³³ B. W. Rowland, *Paper Trade J.* 97, No. 21: 249-250 (Nov. 23, 1933)

¹³⁴ B. W. Rowland, *Paper Trade J.* 97, No. 21: 249-250 (Nov. 23, 1933)

¹³⁵ C. C. Kesler and W. C. Black, *Paper Trade J.* 114, No. 21: 247-250 (May 21, 1942)

tory than when tested in the mill, and hence, reliable indication of the effectiveness of these materials can be obtained only by making tests under mill conditions. The reduced effectiveness of these materials under mill conditions is probably due to greater suction, more violent agitation, etc., obtained on the paper machine compared to laboratory sheet machines. The high speeds and high suction used on machines making kraft papers explains the comparative ineffectiveness of most binders on that grade of paper. Moreover the reduced tearing resistance resulting from the use of binders is also a factor limiting their use in kraft papers.

SHEET FORMATION

The formation of a sheet of paper may be defined as the degree of dispersion of the individual fibers making up the sheet. It is a highly important property and influences many of the properties of the final paper, such as the strength and appearance of the paper, the amount of directionalism in the tensile and tearing strengths, and the amount of expansion and contraction occurring at different moisture contents. Good formation is important on all grades of paper, but it is more important on some than on others. It is particularly important in papers for printing and, generally speaking, good formation is more important in light-weight papers, e.g., carbon tissue, than in heavy papers. Some of the factors to be considered in formation are the amount of two-sidedness of the paper, degree of dispersion or wildness of fibers in the paper, and degree of directionalism of fibers in the paper.

Paper machine conditions have a pronounced effect on the strength of the paper. Sheets made under laboratory conditions are generally much stronger than sheets made from the same stock on the paper machine, because of the different conditions which prevail in the two operations. The flow of stuff on the paper machine wire has a pronounced effect on the dispersion of fibers in the final paper. There are, in addition, other conditions which are responsible for the difference in strength between mill-made paper and laboratory-made paper, such as: (1) the higher consistency used in the mill, which tends to lower the strength; (2) the effect of the shake on the Fourdrinier machine, which affects the distribution of fibers; (3) the presence of unidirectional tension during the pressing and drying of mill-made paper, which prevents it from shrinking in length, thus tending to reduce the strength in the lengthwise direction.

Formation on the paper machine wire is probably the most important single factor affecting sheet strength, the character of the wet pressing and the type of drying being next in importance. Cottrall and Gartshore¹ found that inferior make on the wet end of a Fourdrinier machine results in a loss of strength of the order of 25%. In an ideal system, a dilute suspension of pulp fibers in water should be brought to the wire of the paper ma-

¹ L. G. Cottrall and J. L. Gartshore, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 24: 261-307 (Dec., 1943)

chine in as well-dispersed a condition as possible, with a minimum of alignment or orientation; the stock should have a uniform concentration (consistency), and the long and short, light and heavy fibers should be uniformly distributed throughout the suspension; and finally, a uniform volume of stock should be delivered at a uniform velocity at every increment along the width of the wire. Unless all these conditions are fulfilled, the sheet will be variable in weight, bulk, strength, appearance, and smoothness.

The machine conditions influencing paper properties are discussed in the following sections, under the headings: Dispersion of Fibers in Water; Formation on Paper Machine Wire; Drainage on Paper Machine Wire; Wet Pressing; Drying of Paper; Calendering and Supercalendering. The subject is discussed both for cylinder and for Fourdrinier machines.

Dispersion of Fibers in Water

Since water is universally used for suspending pulp fibers prior to and during sheet formation, it is helpful to know something regarding the fiber-water relationship. Water is held in the stock in several ways. The fibers are suspended in water, but water is also held by capillary attraction between the fibers and in the canals and pores of the fiber. Still a different portion of the water is held in a colloidal state, i.e., as adsorbed water. Beating affects the fiber-water relationship by increasing the amount of imbibed water and, as a result, well-beaten fibers form in a different fashion from unbeaten or partially beaten fibers.

Screening

In order to obtain a uniform dispersion of fibers in water, the stock must be prepared and screened so that it is free of all lumps. The function of the screening operation is to remove large bundles of fiber from the pulp with a minimum loss of good fiber. Unde-fibered stock may come from undercooked chips, wet-strength waste papers, mildewed stock, waste paper which has been scorched, or similar material which is hard to break up, or it may come from lumps of fibers which collect on the sides of chests or in the interior of valves, pumps, or screw conveyors. Screens do not differentiate between dirt and fiber, but they do reject all oversized material.

The screening operations are generally divided into coarse, medium, and fine. Coarse screens or knotters with $\frac{1}{8}$ - to $\frac{1}{4}$ -in. holes are used in the pulp mill to reject all uncooked chips and knots. Rotary screens and set-up screens have been used for this purpose, but recently the Johnsson vibrating screen has come into use because of its gentler screening action and higher capacity. Rotary screens may be used as primary screens on medium grades of paper. These screens have perforations which vary in size from 0.055 in. to 0.125 in., depending upon the grade of pulp. Flat screens

are used as primary screens (when extra clean pulp is desired) and also are generally used for screening the accepted stock from rotary screens. These screens have plates with slots from 0.006 to 0.026 in. in width through which the acceptable fibers must pass. The design and size of the screen plates vary according to the type of pulp being screened. Sulfite pulp is generally screened through screen plates having six to eight slots per inch which range in width from 0.006 to 0.009 inch. Sulfate pulp is generally screened through plates having five to six slots per inch which range in width from 0.010 to 0.014 inch. Board mill stock may be screened through plates having four to five slots per inch and a width of 0.020 to 0.026 inch.

It is possible for flat screens of the finest plate size to pass some fiber bundles, since the slots are several times wider than individual fibers, but the chances of this happening are considerably less than with rotary screens, where the perforations are from 50 to 70 times the diameter of individual fibers. High-grade pulps, in which cleanliness is of prime importance, are often passed over riffles to remove by settling any heavy dirt, such as sand, scale, small knots, and pieces of metal.

Fiber Flocculation

One of the most important factors influencing sheet formation is the way in which pulp fibers disperse in water. If they separate to form individual fibers which remain uniformly dispersed throughout the liquid, the chances are that a well-formed sheet will be produced. On the other hand, if the fibers tend to flocculate and form clumps, the sheet will be wild. To produce a well-formed sheet in which the fibers are randomly oriented, there must be optimum fiber dispersion at the headbox of the paper machine. It is not particularly difficult to separate the fibers into individual units, but it is difficult to maintain a uniform dispersion, since pulp fibers tend to flocculate and form clumps. Campbell² found that a dilute suspension of finely divided cotton linters rapidly formed flocs in a few minutes, even in distilled water.

There are cases where flocculation is desirable as, for example, in the recovery of fiber from white water, where large dosages of alum are sometimes used to help flocculate the fibers before going to the save-all. Flocculation also plays a beneficial role in the retention of fines in the sheet by precipitating the fines on the larger fibers. This is an important factor in groundwood where the fines constitute such a high percentage of the furnish.

Effect of Stock Condition on Flocculation

Flocculation can be explained on the basis of well-known colloidal phenomena. There are certain factors common to all colloidal materials

² W. B. Campbell and F. H. Yorston, Forest Products Laboratory, *Canadian Pulp and Paper Laboratory Quarterly*, April Issue, Review No. 10, pp. 38-43 (1932)

which favor flocculation, and other factors which inhibit flocculation. The fibers in paper stock behave very much as if they constituted a colloidal suspension in that the fibers are held in stable suspension by two forces: (1) an electrokinetic potential, called a zeta potential, between the fibers and the surrounding liquid and (2) by a layer of adsorbed water molecules. Hence, the presence of either a thick layer of water molecules or a high electrokinetic charge prevents flocculation by keeping the individual particles from coming close together. On this basis, a well-beaten stock would be expected to flocculate less than a slightly beaten stock, because the beaten fibers have imbibed more water. Under machine conditions, however, well-beaten stock will generally flocculate more than lightly beaten stock because of the longer time required for the drainage of water from the well-beaten stock. Furthermore, there is mechanical clotting due to physical entanglement of the fibers to consider, and this type of clotting is increased by increased beating of the fibers.³ Many chemists believe that flocculation is mainly mechanical.

Certain fibers are more dispersible by nature than others. Short-fibered stocks are, for example, more dispersible than long-fibered stocks, and hence, flocculation is a relatively minor problem with soda, esparto, or groundwood pulps, and a relatively major problem with cotton, linen, Manila hemp, ramie, or softwood pulps. Long-fibered stocks are frequently cut to shorter lengths in the beater or jordan in order to improve the formation. Fibers containing a high content of hemicelluloses would be expected to flocculate less than fibers with a low hemicellulose content. Bleached pulps generally form better than unbleached pulps, and this is probably due to a difference in the flocculating tendencies of the two pulps.

Campbell⁴ points out that clotting of fibers is caused by eddy currents of low velocity, long fiber length, and high consistencies. Among the factors which Woolwage⁵ found to increase flocculation are: rosin size, gelatinous binders, increased hydration, presence of air, increased fiber length, and very low *pH* or very high *pH*. Among the conditions which he found to increase dispersion are: low consistency, non-gelatinous loadings, agitation, and bleaching of the fibers.

Effect of Electrostatic Charge on Flocculation

Woolwage⁵ found that alum floc, when first added to pulp suspensions, causes flocculation, but after mixing, results in a marked dispersing action. This effect depends upon the amount of alum added. If enough alum is added to neutralize exactly the negative charge on all the fibers, marked

³ S. G. Mason, *Pulp Paper Mag. Canada* 51, No. 5: 93-100 (Apr., 1950)

⁴ W. B. Campbell, *Pulp Paper Research Institute of Canada, Lab. Report No. 75* (Oct. 31, 1946)

⁵ J. C. Woolwage, *Paper Trade J.* 108, No. 12: 149-166 (Mar. 23, 30, 1939)

flocculation would be expected, because the fibers would have no charge to hold them apart. On the other hand, the addition of excess alum would be expected to cause redispersion by reversing the charge on the fibers, giving them all a positive charge.

Erspamer⁶ has illustrated what happens when the electrokinetic charge on the fibers is reversed by means of pyrophosphate. Using a pulp suspension containing alumina, he was able first to flocculate and then redisperse the pulp by increasing the amount of pyrophosphate added. Apparently the pyrophosphate, which gives a negatively charged precipitate, brought the positively charged pulp suspension to the isoelectric point where flocculation took place, and then, upon further addition, redispersed the fibers in the form of a stable negatively charged suspension. Watson and co-workers⁷ found that sodium hexametaphosphate increased the strength of kraft (eucalyptus) handsheets presumably as a result of improved formation resulting from an increased negative charge on the fibers.

Surface-active agents flocculate pulp suspensions according to the relation between the electrical charge of these agents and that on the fibers. Negatively charged surface-active agents flocculate positively charged pulp-alum suspensions,⁶ whereas positively charged surface-active agents enhance the positive charge and thus improve the dispersion. Campbell found that small amounts of univalent electrolytes increased flocculation in groundwood pulp by causing the fines to be precipitated on the larger fibers.

Effect of Gums and Starches on Flocculation

Certain hydrophilic colloids act as powerful dispersing agents for pulp fibers. These materials form a hydrated film on the fiber surface which acts as a lubricant, and they also increase the viscosity of the suspending medium.⁸ Among the agents which have been used, particularly for lightweight tissues, are locust bean gum, deacetylated gum Karaya,⁹ methylcellulose, sodium carboxymethylcellulose, and guar. Because of the strong dispersing action of these substances on pulp fibers, it is possible to obtain sheets of exceptionally good formation from strong, long-fibered pulps, which by themselves would ordinarily produce a wild sheet. These substances bring about an appreciable slowing of the stock on the wire, but the sheet strength is greater than that obtained by beating mechanically to the same slowness. The most favorable effect on formation is obtained in the absence of alum.

When used in ordinary papermaking pulps, about 0.1% locust bean

⁶ A. Erspamer, *Paper Trade J.* 110, No. 24: 321-326 (June 13, 1940)

⁷ W. E. Cohen, G. Farrant and A. J. Watson, *Paper Trade J.* 130, No. 18: 25-26 (May 4, 1950) (Condensation)

⁸ A. Erspamer, *Paper Trade J.* 110, No. 24: 321-326 (June 13, 1940)

⁹ T. R. Lecompte, U. S. 2,069,766 and U. S. 2,088,479 (Feb. 9 and July 27, 1947)

gum based on fiber weight is sufficient to produce an appreciable improvement in formation.^{9a} For specialized, very long fibers such as the Japanese fibers made from kozo, a much higher percentage of gum may be used. Increased beating of the stock increases the retention of the gum and increases its efficiency.

There have been cases where starch has been added for its dispersing effect as, for example, in tissue mills, where as much as 12 to 15% starch on the weight of the pulp has been used to improve formation, but in most cases, starch has a flocculating effect on pulp fibers. Erspamer⁸ found that starch tends to flocculate pulp fibers even in the absence of alum. The flocculating effect of starch would be expected in pulp mixtures containing alum where the negatively charged starch would neutralize the positive charge on the fibers, but the effect is more difficult to explain in the case of plain fiber-water suspensions where both the starch and the fibers normally carry a negative charge.

Effect of Consistency on Flocculation

The consistency at which pulp fibers are made up in water has a pronounced effect on the uniformity of dispersion of the fibers. The higher the consistency, the greater the tendency of the stock to flocculate and produce wild paper. There is a critical value, and when the stock consistency is above this value, the bundles or balls of fibers are large and the dispersion is relatively non-uniform.¹⁰ The critical value for consistency above which the fibers cannot move unimpeded depends upon the type and length of the fibers. Critical values ranging from 0.014 to 0.125% consistency have been worked out by Mason¹¹ based upon the axis ratio of the fiber, that is,

$$\frac{\text{Fiber length}}{\sqrt{(\text{Width}) (\text{Thickness})}} \times \frac{\pi}{2}$$

The consistencies commonly used for forming commercial stocks on the paper machine are as follows:

Grade	Headbox consistency
Tissue	0.10-0.15%
Newsprint	0.55-0.60%
Sulfite bonds	0.50-1.00%
Heavy wrapping papers	0.80-0.90%

Doughty¹² found that the higher the consistency of the stock from which

^{9a} J. W. Swanson, *Tappi* 33, No. 9: 451-462 (Sept., 1950)
¹⁰ J. L. Gray and J. A. Van den Akker, *Paper Trade J.* 118, No. 17: 145-150 (Apr. 27, 1944)
¹¹ S. G. Mason, *Tappi* 33, No. 8: 62A (Aug., 1950)
¹² R. H. Doughty, *Paper Trade J.* 95, No. 10: 111-118 (Sept. 8, 1932)

the sheet is made, the denser the finished sheet, but Cottrall and Gartshore¹³ found that increasing consistency tends to decrease bursting strength.

Effect of Shake on Flocculation

On Fourdrinier machines, the shake is a means of partially overcoming the tendency of fibers to flocculate. Shake is usually more effective on beaten than on unbeaten fibers, because beaten stock remains in a liquid condition longer on the wire than unbeaten fibers, and hence the mechanical agitation of the shake has more opportunity to break up the flocs and mechanically disperse the fibers. It is interesting to postulate that, if it were possible to treat the fibers chemically so that no flocculation takes place, no shake would be necessary and paper of excellent formation could be made at any speed.¹⁴

Flocculation and Retention of Non-Fibrous Components of Furnish

When the pulp suspension is first run on the paper machine wire, there is a short interval during which the finely divided matter passes practically unhindered through the wire. Very soon, however, a mat starts to form and subsequent drainage has to take place through this fibrous mat. The efficiency of this mat as a filter depends upon the thickness of the mat and the slowness of the stock. Sheets made from highly beaten stock retain a higher percentage of fine matter than sheets made from lightly beaten stock, because the pores in the wet mat are smaller in size. For example, Fries and Gaffney¹⁵ showed that white water from highly beaten glassine stock contains a very small proportion of ray cells, compared with the large number of these fine cells contained in the white water from a free stock. Too much suction on the suction boxes and suction couch roll may be responsible for sucking loose some of the fine material which has been deposited in the sheet, thereby resulting in a condition known as two-sidedness.

The retention of the fine colloidal or near colloidal matter presents a problem because it is finer than the pores in the wet fiber mat. This is a problem of great practical importance, because many of these materials (pigments and dyestuffs, for example) constitute the most expensive part of the furnish. The retention of the fine cellulosic matter is important because it adds to the density and strength of the paper. In order to retain this material, it must be flocculated or coflocculated with the larger fibers to increase its effective size. Thus, although flocculation is undesirable for

¹³ L. G. Cottrall and J. L. Gartshore, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 24: 261-307 (Dec., 1943)

¹⁴ F. Frost, *Paper Mill News* 69, No. 26: 20-29 (June 29, 1946)

¹⁵ K. W. Fries and J. D. Gaffney, *Paper Trade J.* 118, No. 12: 101-104 (Mar. 23, 1944)

best formation, it is desirable from the standpoint of increasing the retention.

There are several patented processes for increasing the retention of the non-fibrous constituents of the furnish. Starch in combination with alum and alkali forms a gelatinous floc which helps to retain the starch and other fine materials in the furnish. Animal glue is used in a patented process (Sveen glue process) to increase the retention of the fine material in the furnish. In this process, a high grade glue is dissolved in water, size added, *pH* adjusted with alum, and the solution usually aged at low temperature and a concentration of 1% for about twenty-four hours. During this period, the glue becomes "activated," i.e., it increases in particle size and changes from hydrophilic to hydrophobic.¹⁶ When the activated glue is added to the papermaking stock a few seconds before going to the wire, improved retention and better distribution of the fibers, rosin size, pigments, and dyestuffs are obtained.¹⁷ The process is most effective in furnishes containing fillers, and under good conditions, a reduction of 50% in the solids in the white water has been claimed.¹⁶ Alum is necessary in the process and must be added early in the papermaking process, since good results seemingly depend upon the adsorption of negatively charged glue particles on positively charged alumina floc to bring about an isoelectric condition on the fibers. The amount of glue used is ordinarily less than 0.1% on the weight of the pulp. This activated glue is also used in a special flotation type save-all to be discussed later. The addition of 10 to 20 p.p.m. of activated silica to the pulp before the headbox increases the retention and improves formation. Aluminum ion should be present and usually a *pH* of 5.0 is indication of sufficient aluminum.

Formation on Paper Machine Wire

So far, formation has been discussed from the standpoint of flocculation. It has been pointed out that excessive flocculation of the pulp fibers leads to wildness in the paper. There is another factor in formation to be considered, and that is the problem of directionalism or, in other words, the tendency of the fibers to line up in the machine direction of the paper. This directionalism affects the strength of the paper, as well as its tendency toward curl and, in most cases, is considered undesirable, although a high ratio of machine direction strength to cross direction strength is desirable on certain grades of paper, e.g., spinning and twisting papers.

Effect of Approach Flow on Fiber Orientation

In a well-designed mill, the discharge of stock from the screens to the headbox should be even and free of spouting, since spouting of stock into

¹⁶ P. M. Loddengaard, *Paper Trade J.* 105, No. 9: 133-138 (Aug. 26, 1937)

¹⁷ P. M. Loddengaard and R. Tutt, *Paper Trade J.* 112, No. 22: 263-265 (May 29, 1941)

the headbox results in the inclusion of air and in streams which carry through the slice. Baffles are used in the headbox to retard channeling and turbulence. The problems are not severe at low flows of stocks, but with large flows, special flow spreaders are necessary for best results. It has been found that the flow is more uniform if spreaders are used which reduce the area of spreading at the same time that the width of spreading is increased. The cross-sectional area thus diminishes at the same rate as the longitudinal flow. By maintaining the stock velocity the same at all points across the machine,¹⁸ the approach functions as a hydraulic nozzle which spreads the flow with uniform velocity and without channeling or cross currents. This compressing of the flow can be done in successive stages in a telescopic type flow spreader when large flows are handled. For large machines, the inlet may consist of two ducts which supply stock to both the front and back sides of the machine.

There are many commercial designs for stock inlets, and proponents for each claim that it gives the most uniform flow and stock distribution without undue turbulence, and that it causes the stock to reach the wire in a smooth-flowing stream. This subject is a study in hydrodynamics and is too far afield to warrant a complete discussion in this book.

Effect of Slice on Fiber Orientation

For many years papermakers believed that fibers tend to align themselves in a moving stream. Recent evidence indicates, however, that the distribution of fibers in a moving liquid is nearly random. This random distribution is broken up, however, as the fibers are speeded up under the slice, where the accelerating motion tends to pull the fibers into alignment with the streamlines.¹⁹ Shortly after passing under the slice, the alignment is broken up, which, according to Moss and Bryant,¹⁹ occurs immediately after a double slice and about 6 in. after a single slice. At machine speeds over 500 f.p.m., there is no difference between double and single slices.

The design of the slice is very important. The lip of the slice should be smooth and non-corrosive to minimize disturbance of the stock. Curved slices and rounded slice lips are preferred over vertical slices, and sharp lips because they give less fiber alignment.¹⁹ Upon leaving the slice, the stock should strike the wire slightly beyond the center line of the breast roll.

Since fiber alignment is broken up shortly after the slice, the aligning of fibers in the machine direction must be attributed to a combing effect of the wire on the fibers. In most cases, this results in a greater alignment on

¹⁸ S. T. Weber, *Paper Trade J.* 128, No. 25: 229-230 (June 23, 1949)

¹⁹ L. A. Moss and E. O. Bryant, *Paper Trade J.* 106, No. 15: 226-237 (Apr. 14, 1938)

the wire side of the sheet than on the felt side, although Bailey²⁰ noted more alignment on the felt side.

Effect of Stock Velocity on Formation

The relationship between stock velocity leaving the slice and speed of the wire determines how successive layers are built up in the sheet. If wire speed is appreciably less than stock velocity, the fibers will roll, resulting in forward waves across the sheet. If wire speed is greatly in excess of stock velocity, backward waves will be formed across the sheet, and a combing effect on the fiber results. When uniform fiber distribution is desired, the well-established principle is to maintain stock velocity close to wire speed.²¹ There is some contrary opinion, e.g., Bearce²² who reports that when the stock and wire speeds are roughly equal, the fibers are drawn parallel to the machine direction and set in place almost immediately. Wikland²³ found that the best formation is obtained at a stock velocity at the inlet of 15 f.p.m. slower than the wire speed. If the difference between stock velocity and wire speed is more than 100 f.p.m., it is difficult to make acceptable paper.

The ratio of wire speed to stock velocity must be chosen with regard to the properties desired in the finished paper. A high ratio of wire speed to stock velocity means that a high proportion of the fibers will be drawn into the machine direction. This is desirable in certain grades, e.g., spinning and twisting papers, and hence these papers are made with a relatively low head of stock in the headbox and with a relatively high wire speed. For example, a given paper machine producing twisting paper might operate at a headbox level of 27 inches and a wire speed of 830 f.p.m., whereas the same machine producing a bag paper for which a more equitable distribution of fibers is desired might operate at a head box level of 34 inches and a wire speed of 760 f.p.m.

In an open headbox, the relationship between stock velocity and head of stock behind the slice can be expressed by the following formula:²⁴

$$V = C\sqrt{2gh} \text{ plus the velocity of approach}$$

where V is the velocity of stock in feet per second,

C is a constant equal to 0.95 (slice coefficient),

g is 32.2 f.p.m. (acceleration due to gravity), and

h is the head of stock in feet behind the slice. As an approximation, the formula may be expressed as:

$$h = V^2/2g$$

²⁰ A. J. Bailey, *Paper Trade J.* 101, No. 3: 38-49 (July 18, 1935)

²¹ B. L. Kassing, *Paper Trade J.* 130, No. 24: 87-88 (June 15, 1950)

²² G. D. Bearce, *Paper Trade J.* 100, No. 3: 40-45 (Jan. 17, 1935)

²³ L. G. Wikland, *Norsk Skogsind.* 2, No. 3: 69-76 (Mar., 1948)

²⁴ N. A. Phillips, *Paper Trade J.* 127, No. 22: 502-503 (Nov. 25, 1948)

which shows that doubling the speed of the wire calls for increasing the height of the slice by four times. With the advent of higher machine speeds, special enclosed headboxes equipped with nozzle type slices have come into use for projecting stock onto the wire. The above formula can be used with these slices for calculating stock velocity, except that pressure is used in place of static head and correction factors used for the nozzle design. Slow- to medium-speed machines operate effectively with open slices, but some modern high-speed paper machines are equipped with closed, high-pressure inlets which maintain the required pressure head without the necessity of maintaining an excessively high head of stock.

On high-speed Fourdrinier machines, it is common practice to maintain a certain amount of pitch on the wire by elevating the head end of the machine. This has the effect of increasing the head of the stock and, in theory, accelerates the stock forming the top stratum of the wet fibrous mat. The amount of pitch varies considerably, and on some newsprint machines may amount to almost 1 in. per foot of wire.

Effect of Shake on Formation

The shake on Fourdrinier machines has already been mentioned for its effect in breaking up fiber flocculation. The practical papermaker describes this action of the shake as "closing up" the sheet or, in other words, acting to distribute the fibers more evenly across the wire. This is the principal effect of the shake, although it apparently helps somewhat to distribute the fibers more equitably between the machine and cross directions. Under certain conditions, however, the shake has been reported as increasing the amount of machine direction alignment.²⁵

The shake has more effect on some papers than on others. It is generally considered to be more effective on long-fibered stock and slow stuff than on short-fibered stock and free stuff. It has more effect at high consistencies than at low consistencies. The effect is appreciable on small machines operating at slow to moderate speeds, but there is practically no effect on high-speed machines of great width. In general, the more violent the shake, the greater the effect, although the amplitude and number of strokes per minute must be varied by the machine tender to suit the grade of paper being manufactured. The extent to which the shake of a Fourdrinier machine has operated to break up the machine direction can be fairly accurately determined by a microscopic examination of the paper.

Formation on Cylinder Machines

The problems on a cylinder machine are quite different from those on a Fourdrinier. On cylinder machines, the stock is picked up on a wire-

²⁵ R. Danielsen and B. Steenberg, *Svensk Papperstidn.* 50, No. 13: 301-303 (July 15, 1947)

covered cylinder mold and then transferred to a felt, which carries it to the next cylinder mold. This process is repeated until a multi-ply board of several plies is obtained. It is interesting to note that the felt picks up the first ply of paper and then the wet fiber mat picks up the succeeding plies. The reason paper can be picked up in this manner is that wet paper always adheres to the surface having the denser area, and since both the felt and the paper surface are smoother and denser than the wire covering on the cylinder mold, the wet mat is readily induced to leave the wire.

The deposition of fibers on a cylinder machine takes place as a result of the difference in head between the stock in the cylinder vat and the white water inside the mold. The formation is determined by the static head between the two levels, the area of the mold surface which is submerged in the stock, and by the surface speed of the wire. The higher the head, the more compact the sheet. Another factor which affects the compactness of the sheet is the clearance between the cylinder mold and baffle plate. Generally, this distance is from 3 to 7 in., the shorter distances resulting in a more compact formation.

The consistency of stock in the different vats must not differ too much. Should the difference be too great, there will be a difference in the thickness of the plies, and the thicker ply, which contains a higher percentage of water, will tend to drop off or cause blowing or ply separation. However, up to twice as much stock may ordinarily be carried in one cylinder as in another without serious trouble.

Extreme directionalism is obtained in the case of cylinder papers because of the difference in velocities of the cylinder and the stock.²⁶ Furthermore, there is no shake on a cylinder machine to help distribute the fibers evenly on the wire. One important factor influencing the alignment of fibers is the direction of flow of stock in the vat compared to the direction of rotation of the cylinder mold. The stock flow and mold rotation can be in the same direction or in opposite directions, and both methods are used commercially. When the movement of stock is in the same direction as the mold rotation, a more compact and stronger sheet results, and hence this method is used where strength is important, e.g., tag board. When the stock and mold move in opposite directions, i.e., in the counter-flow vat, the sheet has less grain or machine direction, and this method is therefore used where a minimum of orientation is desired. In the overflow type, large clearances are used between the cylinder mold and the vat in order to permit running large volumes of stock at low consistencies, and the stock is overflowed on the back side of the mold, i.e., on the side opposite to the one where the mold picks up the sheet, to prevent the thickening action which occurs on the uptake side. Other attempts at improving forma-

²⁶ B. L. Kassing, *Paper Trade J.* 130, No. 24: 87-88 (June 15, 1950)

ion have been based upon the use of agitators in the mold or the use of devices to flow the stock across the mold from one end of the vat to the other.

Effect of Wire Marks and Dandy Roll Markings

During the formation of the paper web on the Fourdrinier, a thin layer of fibers is formed on the wire almost immediately, and this thin layer then acts as a filter to hold the remaining fibers and also to retain any "fines" and fillers. The fibers are quite plastic in their swollen and beaten condition and shape themselves to the contour of the wire. Thus, the sheet leaves the wire with a definite surface pattern on one side, called the "wire mark," and the greater the vacuum applied and the more pliable the fibers, the more marked the pattern. On the opposite side, the wet sheet comes into contact with the felt, which leaves a fairly smooth surface, although it is distinct enough in most cases to pass as a felt mark.

The wire and felt marks are partially obliterated in the subsequent wet-pressing and calendering operations, but the pattern still remains to some extent. Even in high-density glassine papers, Wicker²⁷ was able to show that imperfections due to the wire mark exist as residual air voids in the papers corresponding to the recessed areas of the wire mark.

In some cases, a watermark is put into the sheet by means of a dandy, a wire-covered roll with a raised design which presses on the wet sheet. The paper must have a high moisture content to obtain the desired effect. Usually the dandy roll is located between the suction boxes. The dandy roll leaves a depressed design in the sheet which shows up lighter than the rest of the sheet in transmitted light. As a rule, the dandy roll improves formation by "closing up" the top side of the sheet. There is usually some slippage between the dandy roll and the paper which sometimes runs as high as 4%. This results in a drag which disturbs the formation when the machine is run at high speeds. Driven dandys operating at the same speed as the wire eliminate this trouble. In special cases, driven dandy rolls can be operated at different speeds from the wire to obtain unusual watermarks.

Effect of Air and Foam in Stock

Excessive air in the stock results in poor formation by causing surging of the stock in the approach flow system, thus leading to streaks and mottling. Air in the stock tends to become adsorbed on the fibers causing clotting and interfering with felting on the wire.²⁸ The presence of more than 25 p.p.m. of free carbon dioxide is believed to affect seriously sheet formation.

Foam consists of a dispersion of gas (usually air) in a liquid. The size of the bubbles may be less than 1 micron or up to over 100 microns in

²⁷ D. B. Wicker, *Paper Trade J.* 110, No. 1: 8-14 (Jan. 4, 1940)

²⁸ J. A. DeCew, *Paper Trade J.* 100, No. 5: 195-196 (Jan. 31, 1935)

diameter (the latter often called froth). If the system is unstable, the bubbles break, but if they are stable, foam accumulates and causes trouble. Foam is caused by conditions which encourage the formation of bubbles when air is introduced through mixing and agitation. Troublesome foam practically never occurs with pure liquids and is generally caused by surface-active materials which increase the concentration of dissolved substance in the interface. The foam with the smallest bubbles is usually the most stable and the most troublesome.

On Fourdrinier machines, foam tends to collect in the pond of the headbox where it often breaks away and passes on the wire with the stock. On cylinder machines, foam tends to collect in the vats. Foam also tends to collect at the screens and regulating boxes. Foam in the stock at the paper machine screen and approach flow system usually leads to foam spots and poor formation. Ply separation often results in the case of multi-ply boards. Foam spots are produced in the paper when foam bubbles burst on the semi-dried sheet, thereby leaving characteristic circular spots which are more translucent than the rest of the sheet. In filled sheets, foam spots generally contain a larger amount of filler than the surrounding paper, because foam tends to suspend the pigment and later deposit it on the sheet when the foam breaks. This results in a white spot on the sheet if bright pigments are used, or in a color spot if colored pigments are used.

Foam may be caused by a number of factors, such as incomplete wetting of the fibers, excessive amount of water-soluble substances in the furnish, or undue turbulence leading to entrained air. Air usually gets into the stock where the stock cascades over dams or into mix boxes. Leaky pumps also cause foam. With strongly foaming solutions, the volume of foam produced at the beginning is equal to the volume of air whipped into the system, but the foam eventually starts to collapse, and a state of equilibrium is reached. To overcome the difficulty with foam, completely enclosed flow systems are sometimes used with vacuum applied. Foam in pulp suspensions is caused by such substances as dyestuffs, oxidized starches, casein from waste papers, spent cooking liquor in poorly washed pulp, bleach residues, calcium carbonate, and calcium sulfite. Excessive alkalinity of the stock at the beaters and incomplete precipitation of rosin size are other conditions causing foam. Fermentation in the system causes foam. Chlorinated phenols are known to produce stable foam in water systems unless the *pH* is adjusted to the proper range.²⁹

Foam can be dissipated by changing the equilibrium of the system through changes in the interfacial tension. Foam can be destroyed by any substance which is surface active and which displaces the foaming substance from the surface film. Because most anti-foaming agents are not truly

²⁹ C. R. Haefele, *Paper Trade J.* 126, No. 15: 196-198 (Apr. 8, 1948)

water soluble, they must be added in such a way that they do not cause spots in the finished paper. As a general rule, anti-foams should be added as close as possible to the point where the foam is causing trouble. For example, if foam is causing poor formation on the wire, the anti-foaming agent should be added in dilute solution at the machine screen, at the machine headbox, or at the fan pump.³⁰ Kerosene, pine oil, paraffin oil, sulfonated oils, alcohols (octyl, diisobutyl, amyl, and caprylic), fatty acids and fatty acid esters, amides of fatty acids, ethers, organic phosphates, metallic soaps of fatty acids, and silicones are some of the foam inhibitors used by the paper industry.³¹ Usually between 0.01 to 1.0% defoaming agent on the basis of the air-dry pulp is required. Foam killers which are insoluble in water should be added very slowly, and only about 2 to 10 p.p.m. should be used. Care must be taken to select anti-foams which do not lower the sizing of the paper or form spots in the paper. Gentle showers are sometimes used in the headbox of Fourdrinier machines to help in keeping down foam.

Drainage on Paper Machine Wire

Fibers are deposited on the paper machine wire as a result of gravity which pulls the water through the wire and deposits the fibers on the surface of the wire. Table rolls, suction boxes, and suction couch rolls are used on Fourdrinier machines to aid in water removal, and any increase in suction at these points results in an increased rate of drainage and a more compact sheet. On cylinder machines, the fibers are deposited by gravity or suction, although in this case, the head is caused by the difference in liquid levels inside and outside the cylinder mold.

Some of the variables affecting drainage of stock on the wire are temperature, wire size, head above wire, effective suction head, sheet weight, consistency, degree and nature of refining, fiber length, fiber width, fibrillation of fibers, distribution of fines, wet compressibility of pulp pad, degree of hydration, and effect of added chemicals.³² Some of the more important of these factors are discussed in the following sections.

Effect of Fiber Properties on Drainage

Reduction of the comparatively coarse fibers to fine fibrils and fibrillae during beating results in a decrease in the average diameter of the passages in the wet mat when the sheet is laid down on the paper machine wire. This results in a greater increase in the resistance to flow of water through the mat, since flow is dependent upon the number of pores and is inversely pro-

³⁰ W. B. Morehouse, *Paper Trade J.* 120, No. 10: 99-100 (Mar. 8, 1945)

³¹ S. Ross, *Paper-Maker* 119, No. 5: 329-333 (May, 1950)

³² R. W. Reed, *Paper Trade J.* 114, No. 25: 291-297 (June 18, 1942)

portional to the fourth power of the capillary diameter.³³ Short fibers produce wet mats containing small pores even when the fibers are not fibrillated. Hence, the drainage rate is decreased with a decrease in fiber length, although the effect of fiber length is negligible compared with the effect of fibrillation.

The nature of the fiber surface plays an important role in drainage. Reed³² believes that the chemical and physical differences between the "fines" and the longer fibers account for the slower drainage rate of the fines. He found that fiber length per se has only a small effect on drainage rate, and that the difference in drainage rate obtained on different fractions of a pulp fractionated in the Bauer-McNett classifier is due to differences in the chemical and physical properties of the different fractions. Differences in chemical and physical properties explain why groundwood pulps usually have a higher rate of drainage than chemical pulps, even though the fiber length is less.

In a previous section, the effects of flocculation on formation were discussed. Flocculation is also important in drainage, because increased flocculation means that some exceptionally large pores are formed in the wet sheet which bring about a disproportionately high drainage rate. Cations are known to have an effect on drainage.³⁴ Bell found that the addition of electrolytes increased the rate of flow of water through pulp pads. Baird and coworkers³⁵ concluded that non-alkaline electrolytes increase the rate of drainage of pulps. This effect of electrolytes is probably due to a dehydration of the fiber surface and change of electrostatic charge, thereby increasing the amount of flocculation.

It is well known that boiling a pulp suspension increases its drainage rate, due probably to a dehydration of the fiber surface. Tannic acid, which is a strong dehydrating agent, has the same effect. Reed³⁶ found that basic dyestuffs "free" the stock and substantive dyestuffs "slow" the stock when added in substantial percentages. This phenomenon can be attributed to changes which the different dyestuffs bring about in the electrokinetic charge on the fibers. Bleached groundwood forms better than unbleached groundwood,³⁷ probably because of differences in the flocculating tendencies of the two pulps.

³³ W. O. Hisey and C. H. Heigl, *Paper Trade J.* 110, No. 6: 68-74 (Feb. 8, 1940)

³⁴ Summary of paper presented at the Australian Pulp & Paper Ind. Tech. Assoc. Conf. (Feb., 1949), *Pulp Paper Mag. Canada* 50, No. 9: 91 (Aug., 1949)

³⁵ S. R. Adams, F. A. Simmonds and P. K. Baird, *Tech. Assoc. Papers* 22: 482-487 (June, 1939)

³⁶ R. W. Reed, *Paper Trade J.* 114, No. 25: 291-297 (June, 18, 1942)

³⁷ L. A. Beeman, F. C. Goodwill and R. Shearer, *Paper Trade J.* 118, No. 24: 217-220 (June 15, 1944)

Effect of Temperature and Viscosity on Drainage

Drainage time is proportional to the viscosity of the water in which the fibers are suspended.^{38, 39} Drainage time is thus dependent upon water temperature because of the effect of temperature on viscosity. Smith⁴⁰ found that the rate of drainage was about doubled when the temperature was increased from 5 to 30° C. There is enough difference in raw water temperature between the summer and winter months to account for a significant variation in drainage rate, although this difference is somewhat offset by the use of recirculated white water which leads to a more even temperature throughout the year.

Cobb and coworkers⁴¹ point out that the time of drainage is greatly increased at viscosities above 1.5 centipoises. The use of viscous materials in the fiber furnish, such as vegetable gums or high-viscosity starches, tends to slow up the drainage rate.

The Drainage Factor and Specific Drainage Resistance

The drainage factor is defined as the drainage time in seconds per gram of pulp at 20° C. under standard conditions. It can be determined by forming sheets on a British standard sheet machine under standard conditions and taking the drainage time and weight of the test sheets. The drainage factor is the slope of the line produced when drainage time (at 20° C.) is plotted against weight of stock added to the sheet machine.

Specific drainage resistance is a fundamental property based upon Poiseuille's equation. It is based upon the equation for the rate of flow through a fibrous mat, which Campbell expresses as follows:⁴²

$$\frac{Q}{A} = \frac{P}{RW\eta}$$

where Q is the rate of flow through area A , P is the pressure causing flow, η is the viscosity of liquid, W is the weight per unit of area of mass, and R is the specific resistance per unit of weight of the fibrous mass.

Unlike the freeness test, specific drainage resistance has a definite physical meaning. It shows a marked relationship with drainage factor, particularly in the case of slow pulps, indicating that the two properties measure substantially the same pulp characteristics. There is, however, no

³⁸ D. S. Davis, *Paper Trade J.* 91, No. 21: 49-50 (Nov. 20, 1930)

³⁹ R. W. Reed, *Paper Trade J.* 114, No. 25: 291-297 (June 18, 1942)

⁴⁰ Sigurd Smith, "The Action of the Beater," translated by R. Marx, London, Tech. Sec. of the Paper Makers' Assoc. Gt. Britain Ireland (1923)

⁴¹ R. M. Cobb, D. V. Lowe, E. Pohl and W. Weiss, *Paper Trade J.* 105, No. 7: 105-108 (Aug. 12, 1937)

⁴² W. B. Campbell, *Pulp Paper Mag. Canada* 48, No. 3: 103-109, Convention Issue (1947)

positive relationship with freeness, particularly in the range of low freeness values.

Specific drainage resistance is dependent upon the number of pores in the wet sheet and the fourth power of the diameter of these pores.⁴³ According to Campbell, the specific resistance (R) of the pulp mat is composed of two factors,⁴⁴ specific surface of the pulp and volume concentration of pulp in the fibrous mat. Specific surface is directly a pulp property. Volume concentration is not a pulp property since it is determined by two components, compressibility of the pulp and pressure to which the pulp is subjected. However, if the amount of pressing is kept constant, then the principal factor affecting volume concentration is the compressibility of the pulp. Hisey and Matchuk⁴⁵ have shown that both specific drainage resistance and drainage factor of mechanical pulps are directly related to the compressibility factor.

The conditions used in measuring drainage factor come closer to conditions on the paper machine than those used in the freeness test because of the greater head of stock used in measuring drainage factor compared with that used in the freeness tester. This greater head of stock results in greater compression of the pulp pad, more nearly equivalent to that which prevails on the paper machine. Thus, the difference in compressibility of pulps accounts for the discrepancy often noticed between freeness values (obtained in the freeness tester) and drainage factor or drainage time (obtained on the British sheet machine). Differences in compressibility accounts for the fact that groundwood pulp (with low compressibility) may test less free than a beaten sulfite pulp in the freeness test, but act more free on the paper machine. Reed⁴⁶ lists the relative compressibility of different pulps as follows: sulfate, 0.71; soda, 0.50; sulfite, 0.62; groundwood, 0.46.

Water Removal at Table Rolls

Paper machine wires are woven from fine copper or alloy wire. They vary in mesh and also in the style of weave. Two of the several different types of weave used by wire manufacturers are the standard or plain weave, in which the shute is woven over and under alternate warp wires, and the long crimp wire, in which the shute is woven over two warp wires and under the third. The standard or plain weave is used mostly in making bond, book, and other high-grade papers, whereas the long crimp wire is used mostly for making news and kraft papers.

⁴³ W. O. Hisey and C. H. Heigl, *Paper Trade J.* 110, No. 6: 68-74 (Feb. 8, 1940)

⁴⁴ W. B. Campbell, *Pulp Paper Mag. Canada* 48, No. 3: 103-109, Convention Issue (1947)

⁴⁵ W. O. Hisey and K. Matchuk, *Paper Trade J.* 113, No. 12: 131-136 (Sept. 18, 1941)

⁴⁶ R. W. Reed, *Paper Trade J.* 114, No. 25: 291-297 (June 18, 1942)

The standard mesh wires and the grades of paper on which they are generally used are given below.

Mesh	Actual count	Grade of paper
55	55 × 38	Coarse paper, such as newsprint, and wrappings
60	60 × 40	Coarse paper, such as newsprint, and wrappings
65	65 × 44	Medium grades
70	70 × 52	Medium grades
75	75 × 56	Fine book papers
80	80 × 60	Fine book papers

Special papers may require a finer mesh than 80 × 60. On cylinder machines, it is common practice to use a 40- or 50-mesh wire for the filler stock, and a 50- or 60-mesh wire for the liner stock. As a general rule, the finer mesh wires have the shorter wire life. Fine mesh wires result in slower drainage rate because they catch more of the fines and hence build up a denser sheet.⁴⁷

When the stock first flows on the wire, the water passes readily through the wire because there is relatively little resistance to flow at this point. The force responsible for draining the water through the wire is the head of stock on the wire and the action of the table rolls revolving underneath the wire. These rolls create a suction by the small "wedge" of water formed where the roll leaves the wire. This wedge of water tends to pull water from the sheet by (1) a hydraulic effect as a suction leg and (2) a surface tension effect.⁴⁸ Campbell has estimated that the suction effect varies from about 0.04 to 0.12 cm., compared with a total pressure head starting at about 1.2 cm.

The effectiveness of the table rolls increases at higher machine speeds because of the greater suction created at higher speeds. The suction at high speeds is so great that it has been necessary on very fast machines to use slow stock to prevent "flooding" of the table rolls. In addition, on very high-speed machines (e.g., newsprint machines), it may be necessary to eliminate some of the table rolls and replace them with wire-covered or grooved rolls which support the wire, but do not cause much water removal. Forming boards may be used at the beginning of the wire on high speed machines where they support the wire and scrape water from the bottom of the wire. One type of high-speed (2,000 f.p.m.) tissue machine uses no table rolls. Instead, a suction breast roll is used equipped with two suction boxes. The first box pulls the water into the breast roll and the second box holds it there, after which it is thrown out of the roll just below the wire. The sheet is completely formed within a few inches of the breast roll.

⁴⁷ H. Specht, *Paper Trade J.* 104, No. 8: 92-95 (Feb. 25, 1937)

⁴⁸ W. B. Campbell, *Pulp Paper Mag. Canada* 48, No. 3: 103-109, Convention Issue (1947)

At speeds of 1,200 to 1,400 f.p.m. and over, the use of table rolls causes trouble by "whipping" and splashing water back through the wire, thereby disturbing the formation. Smith⁴⁹ believes that two-sidedness is caused by a washing or flooding of the underside of the wet sheet every time the sheet passes over a table roll. This is due to water following the roll into the nip where the water momentarily raises the whole sheet, flooding and loosening the fine fibers and fillers, which are then almost immediately withdrawn by the suction created by the rolls as they part from the wire surface. Grooved table rolls or deflectors may be used to prevent splashing of water through the wet sheet.

Wear on the wire at high speeds is considerable because of the pull on the wire at each roll. For this reason, flexible wires made from fine wire are required on high-speed machines.

Water Removal at Suction Boxes

As the sheet progresses down the wire, it passes over a series of suction boxes which remove large quantities of water from the paper. Even though the stock has lost approximately 75% of its original water before reaching the suction boxes, it still contains about 97 to 99% moisture at the time it reaches the first suction box. The suction boxes remove a good part of the remaining water and, at the same time, compact the sheet.

Suction boxes provide a very effective means of water removal, since they provide a vertical pressure which does not disturb the formation of the sheet. The number of suction boxes varies from 2 to 10, depending upon the grade of paper. Most glassine is made on machines having 6 to 10 suction boxes. The suction boxes should be in good mechanical condition and should be large enough to take care of the flow of water. The vacuum is usually maintained at 5 to 11 in. of mercury. In addition, a vacuum of 12 to 15 in. is maintained at the suction couch roll. Greater suction than this is considered bad practice, since it puts too much strain on the wire.

Reuse of White Water

When papermaking stock is run on the paper machine wire, a certain amount of the solid matter is not retained, but is passed through the wire, together with most of the water used for suspending the fibers. The water removed from the stock on the wire is known as "white water."

Twenty-five years ago, it was generally believed that white water could not be reused without sacrificing too much of the quality of high-grade papers. Today, however, all mills practice some degree of white water reuse. Some of the reasons for practicing white water reuse are: (1) to conserve water, (2) to reduce the amount of waste from the mill in order to meet

⁴⁹ F. Smith, *Paper Trade J.* 129, No. 21: 468-470 (Nov. 24, 1949)

state or federal standards regarding stream pollution, (3) to conserve fiber and other raw materials which are carried away in the white water, and (4) to conserve heat.

To reuse effectively white water in sprays and showers, the fibers and other suspended matter in the water must be removed. In spite of the advantages of white water recovery, many mills still find it necessary to run part of the white water to the sewer in order to prevent the accumulation of dissolved substances in the paper mill system. These substances, if allowed to accumulate indefinitely, tend to cause trouble with foaming, slime growth, poor sizing, and sticking on the press rolls. The recent introduction of improved anti-foaming agents and new toxicants has improved the situation and made it possible to reuse upwards of 100% of the white water, except in those mills where there are frequent changes in product or a wide variety in colors. Even if the water is not going to be reused, the water should be treated to recover the valuable solids in the water.

Among the several methods of fiber recovery are inclined screens, sedimentation basins, rotary screen and vacuum filter save-alls, settling save-alls, flotation save-alls, and precoated rotary filters. These are discussed in the following sections. The efficiency of recovery of solid matter depends upon the type of save-all and the ratio of fibrous to non-fibrous constituents in the water. In a well-run paper mill, the water leaving the mill should contain less than 0.7 lb. of fibrous material per 1,000 gal., and with the recent trends toward more stringent controls, about 0.3 lb. per 1,000 gal. (25 p.p.m.) is more desirable. In some cases, the losses can be reduced to 0.15 lb. per 1,000 gal.^{50, 51} According to Skinner,⁵² the fiber losses from paper mills should not exceed 1%, but it is doubtful if many mills meet this requirement.

In making a mill survey of sewer losses, total flow should be determined first, using Venturis, orifice plates, weirs, or flumes. Samples of water for analysis should then be taken at various intervals proportionate to the flow so that truly representative samples are obtained.

Composition of White Water

The composition of the white water depends upon the type of stock, type of non-fibrous furnish, size of the wire, and amount of suction used on the wet sheet. Ordinarily, white water contains fiber debris, small fibers, soluble matter, and a high percentage of non-fibrous suspended matter such as pigments, starches, and dyestuffs. Usually the ratio of finely divided matter (filler and fiber debris) to fiber is higher in white water than

⁵⁰ P. M. Loddengaard, *Tech. Assoc. Papers* 20: 291-298 (June, 1937)

⁵¹ S. B. Applebaum, *Paper Trade J.* 122, No. 23: 249-251 (June 6, 1946)

⁵² H. J. Skinner, *Ind. Eng. Chem.* 31, No. 11: 1331-1335 (Nov., 1939)

in the original furnish. The total amount of solid matter in the white water varies greatly from mill to mill, depending upon the grade of paper and method of white water treatment. Table I shows the amount of solids present in white water from a mill making filled grades of printing and writing papers.⁵³ White water from unfilled papers contains much lower percentages of solid matter than indicated in this table.

TABLE I
SOLIDS PRESENT IN WHITE WATER FROM MACHINE MAKING PRINTING
AND WRITING PAPERS

Machine speed 700 f.p.m.	
Paper grade	Solids, lb./1,000 gal.
Book paper (19% ash)	34.3
Light-weight bond (6.5% ash)	13.0
Offset (11% ash)	26.4
Coating base stock (8-10% ash)	12.6
Mimeo (12% ash)	18.3

The composition of white water depends upon its source on the paper machine. The richest white water is obtained from the trays under the first part of the Fourdrinier wire. This rich tray water is generally returned directly to the mixing box, beaters or other points as make-up water. A less rich white water is obtained from the pit under the wire. In some mills, the pit is divided into sections to collect water of different richness, with the richest used directly as make-up and any excess or less rich water sent to save-alls. Thick stock from breaks at the couch roll is generally collected separately in the couch pit and sent directly to the machine chest as make-up.

In analyzing white waters, the following tests are important.

- Total suspended solids* are measured by filtering the white water through a qualitative filter paper on a Buchner funnel and weighing the contents on the filter paper.
- Fixed suspended solids* (mostly fillers) are measured by weighing the amount of material left after ignition of the filter paper and contents.
- Combustible suspended solids* (mostly fibers) are measured by subtracting the fixed suspended solids from the total suspended solids.
- Total dissolved solids* are measured by evaporating some of the filtered white water to dryness and calculating weight of residue in pounds per gallon. A blank on fresh water should be subtracted to give the amount of dissolved solids resulting from the furnish.
- Fixed dissolved solids* are measured by igniting the total dissolved solids and weighing the ignited residue.
- Combustible dissolved solids* are measured by subtracting the amount of fixed dissolved solids from the total amount of dissolved solids.

⁵³ W. P. Nesbitt, *Pulp Paper Mag. Canada* 51, No. 4: 82-85 (Mar., 1950)

Inclined Wire Screens as Save-Alls

The inclined wire screen is a very crude device which has been used as a save-all. It is not very effective in removing suspended matter, and the effluent from the screen cannot be reused except for stock dilution. Mills using this type of save-all generally run the excess effluent to the sewer.

Settling Basins as Save-Alls

Settling basins, in which the white water is held before reuse, are somewhat more effective than inclined wire screens. The effluent is generally used only for stock dilution, which means that there is considerable loss of water. Some of the disadvantages of sedimentation basins are the large space requirements and long retention period required which lead to slime troubles and the accumulation of dirt in the water.

Rotary Screen and Vacuum Filter Save-Alls

The revolving screen type of save-all may be one of two types, the simple screen type or the vacuum type. The simple screen type consists of a wire-covered cylinder which revolves in a vat containing the white water. A fiber mat is formed on the wire, due to a difference in head between the water levels inside and outside the cylinder. The efficiency of this type of save-all is low, except where the water contains long fibers or where a fiber mat is used as a precoat on the filter.

The vacuum filter type of save-all is more efficient than the simple screen type. It produces high clarity water which contains about 1.0 to 2.0 lb. of total suspended solids per 1,000 gal., none of which is long fiber.^{54, 55} According to Rudolfs and Axe,⁵⁶ the average reduction of suspended solids by vacuum filtration is about 50%, although this varies from 20 to 70%, depending upon the length of the fiber in the white water. In filtering white water containing a high filler content, it is advantageous to add some long-fibered stock to the water in order to produce a more efficient filter mat.

Sedimentation Type Save-Alls

Sedimentation type save-alls operate on the same principles used in the sedimentation of raw water. The white water is first treated with coagulant to flocculate the finely suspended matter, which is then settled out in basins equipped for the continuous removal of sludge. This type of save-all is much more efficient than the filtration types, particularly when the white water contains a high filler content, e.g., in book mills.

⁵⁴ H. A. Morrison, *Paper Trade J.* 122, No. 15: 155-157 (Apr. 11, 1946)

⁵⁵ R. S. Hawley, *Sewage Works J.* 11: 512-517 (1939)

⁵⁶ W. Rudolfs and E. Axe, *Paper Trade J.* 125, No. 3: 31-36 (July 17, 1947)

Alum and alkali are used as coagulants in sedimentation save-alls. Some white waters contain sufficient alum (added in sizing operation), but usually extra alkali (usually lime) to the extent of 1.0 to 1.5 lb. per 1,000 gal. must be added for best results. In some mills, extra alum is added to the extent of 2.0 to 3.0 lb. per 1,000 gal. The optimum pH is around 5.0 to 6.0. Other chemicals, e.g., special starches or activated silica, are frequently added with the alum.

In one type of sedimentation save-all, the white water is caused to fall upon a cone prior to its entry into the sedimentation chamber to remove air bubbles adhering to the suspended particles. According to Benson and Brakewood,⁵⁷ this sedimentation save-all reduces the amount of suspended matter from 2.7 lb. per 1,000 gal. in the influent to only 0.26 lb. of suspended matter per 1,000 gal. in the effluent. The sludge contains about 5.0 lb. of solid matter per 1,000 gal.

In another process, called the "sludge contact process," a depth of previously accumulated suspended solids of about 7 to 8 ft. is maintained in the reactor in order to contact the incoming chemically treated white water. In this process, a controlled amount of alum (about 2 grains per gallon for sized papers and about 10 grains per gallon for unsized and heavily filled papers) and sometimes soda ash (about 2 grains per gallon) are added to the white water just as it enters the reactor. In addition, about 5 to 10 p.p.m. of activated silica may be added to aid in forming a more compact sludge. The intimate contact of the incoming treated water with the previously accumulated sludge tends to filter out and more effectively coagulate the solid matter in the water, since any newly formed precipitates tend to adhere to the previously formed precipitates, thus increasing the size of the particle. Gentle mixing is provided to aid in floc formation and also to maintain a uniform concentration of sludge. That part of the sludge which settles rapidly is drawn off at the bottom of the settling tank at a consistency of about 1%, while the clarified white water is removed by decanting. The slower settling precipitate is drawn back into the mixing zone to aid in the formation of new precipitates. According to Calise,⁵⁸ the effluent from the reactor never exceeds 0.3 lb. of fiber per 1,000 gal. under normal operating conditions, and the results are far superior to those obtained by ordinary coagulation and settling without contact with previously accumulated sludge. In one installation⁵⁹ raw white water containing 2 to 3 lb. of fiber per 1,000 gal. was reduced to 0.1 lb. per 1,000 gal. In another installation in a liner board mill, the suspended solids in the white water were reduced from 4.5 lb. per 1,000 gal. to 0.25 lb. per 1,000 gal. and, at

⁵⁷ C. A. Benson and H. E. Brakewood, *Paper Trade J.* 124, No. 17: 86-88 (Apr. 24, 1947)

⁵⁸ V. J. Calise, *Paper Trade J.* 127, No. 7: 352-356 (Aug. 12, 1948)

⁵⁹ J. M. Kahn, *Paper Trade J.* 127, No. 24: 512-513 (Dec. 9, 1948)

the same time; the color was reduced from 250 to 28 and the five-day B.O.D. reduced from 128 p.p.m. to 62 p.p.m.

Flotation Type Save-Alls

Flotation type save-alls are based upon the principle that solid particles will rise to the surface of a liquid if the liquid is loaded with air. Thus, in this type of save-all, air is mixed with the waste water so that free air bubbles are produced when the pressure is reduced. When the air is properly introduced, the bubbles attach themselves to the floc and its occluded material, and later, when the air is released, these bubbles cause the material to float to the surface. The floated fiber is then removed by skimming.

There are two types of flotation save-alls, those that operate under reduced pressure (Adka or Savalla) and those that operate at atmospheric pressure (Sveen-Pedersen). In general, flotation save-alls have the advantage of requiring very little space because of their low retention time. They have the disadvantage of not working well on waters containing a high percentage of fillers or other heavy material.

Adka Save-All. The Adka save-all operates under reduced pressure. The white water is first forced through an air injector at high velocity to saturate the white water with air at atmospheric pressure. Then, the water is mixed with chemicals in an open-flow box where the undissolved air escapes as froth. The velocity is then decreased to permit flocculation, and the mixture is finally drawn into a sealed tank where a partial vacuum is applied. As the pressure is reduced, dissolved air separates in the form of minute bubbles which adhere to the flocs and draw them to the surface where they are removed.

If the suspended particles are so small that the air bubbles do not adhere well, it is necessary to resort to chemical coagulation of the water. Alum, caustic soda, activated silica, rosin size, and sodium aluminate are some of the coagulants used. Poor and Whitenight⁶⁰ describe the use of fatty acids which promote flocculation by reacting with aluminum ions in the water to form insoluble soaps. They found the shorter chain acids (up through myristic) to be more effective than the longer chain acids.

The Adka save-all is very efficient in recovering fibers and will readily reduce the white water solids in ordinary cases to 0.2 to 0.3 lb. per 1,000 gal. It is not so efficient in recovering fillers, and will not remove coloring matter adsorbed on fillers. When flocculating agents are used, the presence of about 10 to 20% filler enhances the tendency toward agglomeration.⁶¹ Poor and Whitenight⁶⁰ found that clay and titanium dioxide are

⁶⁰ E. N. Poor and H. A. Whitenight, *Paper Trade J.* 114, No. 9: 101-104 (Feb. 26, 1942)

⁶¹ E. N. Poor, *Paper Trade J.* 110, No. 10: 143-144 (Mar. 7, 1940)

more easily flocculated with fatty acids than talc or asbestine. The recovered stock can be returned to the beater, decker, wire pit, or even back to the fan pump.⁶²

Sveen-Pedersen Save-All. The Sveen-Pedersen save-all operates at atmospheric pressure. In this process, the white water is first pumped under pressure (40–60 p.s.i.) to a retention chamber where air, about 1% by volume, is introduced. From there, the water is pumped into the save-all where the release of pressure at this point produces air bubbles which carry fiber and filler particles to the surface where they are skimmed off. Before entering the save-all, a special colloidal glue is sometimes added to stabilize the foam and provide greater air buoyancy. For light-weight sheets, a glue dosage of 2 p.p.m. (0.5 lb. per ton of paper) is typical, and for heavy sheets, a dosage of 4 p.p.m. (1.0 lb. per ton) is typical.⁶³ Activated silica sol may be used in place of glue.

TABLE II
TYPICAL RESULTS WITH SVEEN-PEDERSEN SAVE-ALL
Amounts in pounds per 1,000 gallons

Type of paper	Solid matter	
	Into save-all	Out of save-all
Chipboard	1.6– 2.5	0.08–0.30
Liner board	2.6– 3.6	0.08–0.25
Book—clay	7.2–17.9	0.10–0.31
Book—carbonate	12.5–38.2	0.19–0.40
Bond—wood	4.0–12.4	0.12–0.29
Newsprint	7.0– 9.2	0.17–0.38
Tissue—toilet	2.6– 5.8	0.14–0.27

Aluminum ion is essential to the proper operation of the Sveen-Pedersen save-all to give the air bubbles a positive charge so that they will attach themselves more readily to the negatively charged agglomerates.⁶⁴ White water containing from 15 to 17 p.p.m. of aluminum ion is satisfactory. Additional aluminum ion can be added if necessary, but must be added an appreciable length of time before the water enters the save-all.⁶³ The save-all operates satisfactorily at pH values between 4.2 and 7.3.^{63, 65}

Effluents as low as 0.1 to 0.2 lb. of solids per 1,000 gal. are obtained on water from unfilled papers, and about 0.2 to 0.4 lb. per 1,000 gal. on water from filled papers.^{66, 67} Typical results on a number of different grades of paper are shown in Table II.⁶⁸ As a general rule, the recovered fiber and

⁶² B. Nibberger and R. E. Bodette, *Tappi* 32, No. 12: 574–576 (Dec., 1949)

⁶³ H. R. Clodfelter, *Pulp & Paper* 21, No. 10: 54–58 (Sept., 1947)

⁶⁴ W. D. Harrison, *Paper Trade J.* 109, No. 7: 67–72 (Aug. 17, 1939)

⁶⁵ P. Easton and R. Baum, *Tappi* 33, No. 6: 301–304 (June, 1950)

⁶⁶ R. T. Sheen, *Paper Trade J.* 126, No. 9: 117–121 (Feb. 26, 1948)

⁶⁷ W. D. Harrison, *Paper Trade J.* 109, No. 7: 67–72 (Aug. 17, 1939)

⁶⁸ O. F. Hutchinson, *Paper Trade J.* 127, No. 23: 44–49 (Dec. 2, 1948)

filler (at 2 to 3% solids) are returned to the stock system, preferably as close to the paper machine as possible. The clarified water is withdrawn through tubes in the bottom of the unit into a storage chamber from which it is pumped to the showers, regulators, and beaters.

Precoated Rotary Filters

A special type of filter, known as the Waco filter, is widely used in European mills and in a few American mills as a paper mill white water save-all.⁶⁹ This type of filter operates on a strictly mechanical basis, no pH adjustment or added chemicals being required. A preformed cellulose mat is used as the filter. This is continuously formed on a traveling wire prior to the filtering operation, after which the wire carrying the preformed mat (containing about 0.025 lb. of fiber per square foot of exposed wire surface) is passed around the main cylinder (diameter 78 in.) in a vat. The white water flows through the mat and wire into the interior of the cylinder while the suspended matter is retained on the fiber mat. As the wire leaves the cylinder, the mat and recovered material are doctored off and returned to the system. An average efficiency of about 92 to 97.5% has been reported on filled papers in a mill making bond and book papers containing 6.5 to 19% ash.⁶⁹

Wet Pressing

Upon leaving the couch roll, the moisture content of the paper is about 18 to 22% for light-weight papers made on fast machines (1,500 f.p.m.), and about 20 to 22% for heavy kraft board made at speeds of about 1,300 f.p.m.⁷⁰ The next step in the papermaking process is to reduce the moisture content of the paper by wet pressing without adversely affecting the quality of the paper. Wet pressing may be regarded as a continuation of water removal already begun on the machine wire.

Types of Presses Used

On Fourdrinier machines, the wet sheet is passed through one or two set of press rolls and then the sheet is reversed and sent through another set of rolls. On cylinder machines, a series of small press rolls, called baby press rolls, is used at gradually increasing pressure before passing through the main press rolls. During the pressing operation, the sheet expands in a lateral direction.

Felts are commonly used on the wet press section to help support the sheet and help in removing the water by acting as an absorbing medium.

⁶⁹ W. P. Nesbitt, *Pulp Paper Mag. Canada* 51, No. 4: 82-85 (Mar., 1950)

⁷⁰ C. Clark, *Paper Ind.* 30, No. 11: 1615-1617 (Feb., 1949)

The felts should be porous enough to allow rapid water removal, but not so porous that they are lacking in strength. Hard, closely woven felts tend to put more pressure on the sheet than porous felts. The felts used on high-grade papers are closer in texture and softer than those used on coarse papers. All felts should be uniform in texture and should not be subjected to unusual strain so that they wear unevenly. The method of running the felts in the first press section on cylinder machines is quite important. Felts may be run around both the top and bottom press roll, or the top press roll may be run bare. The latter arrangement produces a sheet of higher finish, but reduces the strength and is likely to cause crushing of the sheet.

The early presses used plain rolls in which the water was forced out of the sheet by pressure. With this arrangement, the water flows back over and through the sheet, and the incoming sheet is carried through a flood of the liquid which has been pressed out of the sheet. When plain presses are used, the top press roll is usually made of wood, granite, brass or hard-rubber composition, while the bottom press roll is usually rubber covered. Rubber rolls have the advantage of increasing the width of the nip, thus decreasing the specific pressure but increasing the time of pressing. The softer the rubber used in the covering, the more pronounced this effect, so that the hardness of the rubber used is an important variable.

Within recent times, suction press rolls have come into general use. These consist of a top press roll of solid construction and a lower press roll which is operated under suction. The bottom press roll, which is frequently rubber covered, is perforated with holes (usually $5/32$ in. in diameter) through which the suction is applied. With such an arrangement, it is possible to remove water through the sheet more or less vertically so that a greater amount of water can be removed without disturbing the formation of the sheet. Suction press rolls tend to keep the felts from filling up.

Press rolls are normally crowned or, in other words, the rolls are ground so that their diameter is larger at the center than at the ends. Crowning of press rolls is necessary to offset the natural sagging which occurs in the rolls. In some cases, crowning is done to provide less pressure on the edges of the sheet so that more moisture is carried into the driers to offset the faster drying at the edges of the paper. The crown may be ground into either the top or the bottom roll, or divided between the two rolls. The amount and evenness of crown can be checked by examination of the impression obtained when the press rolls are lowered onto a sheet of paper placed over a sheet of carbon paper. The amount of crown to be used depends upon the diameter and width of the press rolls. The amount of rubber covering on the press rolls is also a factor, since rolls with soft and thick rubber coverings require substantially more crown than rolls with

hard and thin rubber coverings.⁷¹ Non-deflecting press rolls which require no crowning have recently been developed.⁷²

Variables in Wet Pressing

The pressure used in wet pressing is opposed by the slight resistance of the fibers to deformation and the resistance of water to flow through the fine capillaries of the wet fibrous mat. In other words, part of the pressure is used to compact the sheet and part is consumed in liquid flow, much more of the pressure being used in liquid flow than in compacting the sheet. As the paper web is compressed, the resistance to liquid flow becomes increasingly great because of the reduction in the size of the pores in the paper.

The removal of water at the presses is determined by (1) pressure applied per square inch of contact area, (2) length of time pressure is applied, (3) number of presses, (4) type of press (suction or plain), (5) absorbency of press felts, (6) viscosity (due to changes in temperature) of water, and (7) porosity of wet web. Campbell⁷³ states that over a considerable range above 12% consistency, the increase in sheet dryness with pressure is approximately proportional to the pressure used and to the time of pressing. It is inversely proportional to the square of the basis weight, to the square of the specific surface of the stock, and to the viscosity of the water. The effect of these variables on sheet consistency can thus be expressed by the following formula:

$$Pt/W^2S^2\eta$$

where P is the applied pressure per unit of area, t is the time during which the pressure is applied, W is weight per unit of area (basis weight), S is the specific surface (surface to volume of the stock), and η is the viscosity of the water at the temperature used.

Pressure used in pressing may be expressed as (1) total pressure applied, (2) pressure per lineal inch of nip, or (3) pressure per square inch of contact. The total pressure is that due to the weight of the top press roll plus any weight added by mechanical means (by added weights and levers or by pneumatic loading). The pressure in pounds per lineal inch of nip is the total pressure divided by the length of the nip. All these methods of expressing pressure are used, but the most important fundamental measure of pressure is the pressure per square inch of nip. This varies from a maximum at the center of the nip to zero at the beginning and end of the nip, but the average pressure per square inch of nip area can be calculated from the total weight per lineal inch of nip and the nip width. The nip width is

⁷¹ F. A. Garrett, *Pulp Paper Mag. Canada* 46, No. 3: 185-198, 204, Sixth War-time Issue (1945)

⁷² J. V. Edge, *Paper Ind.* 31, No. 9: 1120 (Dec., 1949)

⁷³ W. B. Campbell, *Pulp Paper Mag. Canada* 48, No. 3: 103-109, Convention Issue (1947)

not easily calculated, since it varies directly with the square root of the pressure (pounds per lineal inch), roll plasticity, and thickness of roll covering.⁷⁴ It is directly proportional to the diameter of the rolls if both rolls have the same diameter, but not if the rolls have different diameters.

The time of pressing is directly proportional to the nip width and inversely proportional to the speed of the paper web. Thus, if the machine speed is doubled, either the pressure per square inch of contact area or the nip contact area must be doubled, or each increased proportionately.

The results of Jahn and coworkers⁷⁵ have shown that the amount of water retained by a pad of wet beaten pulp at any constant time of pressing is greatly affected by the pressure applied up to a pressure of 3,000 p.s.i. In this work, the equilibrium moisture content of the pulp mat was found to vary from about 78% moisture at a pressure of 500 p.s.i. to a moisture content of 35% at a pressure of 3,000 p.s.i. This equilibrium moisture content (35%) at 3,000 lb. is very close to the fiber saturation point. However, the equilibrium moisture content is never reached during pressing of the wet sheet on the paper machine because of the long time required to reach the equilibrium point. For example, Bell⁷⁶ found that it took fourteen days for equilibrium to be reached when beaten pulp sheets were subjected to a pressure of 200 p.s.i., and Jahn and coworkers⁷⁵ found that four hours were required at pressures of 4,000 p.s.i. Water is removed more slowly from well-beaten stock than from free or unbeaten stock, and consequently, well-beaten stock generally has a somewhat higher moisture content leaving the wet press section.

Water is more easily pressed out of the sheet at higher temperatures than at low temperatures, due to the lower viscosity of the water at high temperatures. Increasing the temperature of the water 1° C. increases the fluidity about 2½%.⁷⁷ Stamm⁷⁸ found that raising the temperature of the wet sheet from 65 to 85° F. during pressing reduces the moisture content of the paper going to the driers by 2 to 3%. Some mills pass the paper over two to three driers between the second and third presses to aid in water removal.

Effect of Pressing on Sheet Properties

Pressing causes a lateral or sliding movement of the fibers from the high spots to the low spots of the sheet. This increases the smoothness of

⁷⁴ W. G. McNaughton, *Paper Trade J.* 115, No. 9: 97-104 (Aug. 27, 1942)

⁷⁵ A. Sedoff, C. V. Holmberg and E. C. Jahn, *Paper Trade J.* 109, No. 26: 350-357 (Dec. 28, 1939)

⁷⁶ J. H. B. Bell, *J. Soc. Chem. Ind.* 52, No. 17: TS109-116; No. 18: TS119-130 (Apr. 28, May 5, 1933)

⁷⁷ W. B. Campbell, *Pulp Paper Mag. Canada* 48, No. 3: 103-109, Convention Issue (1947)

⁷⁸ F. C. Stamm, *Paper Trade J.* 100, No. 2: 20-22 (Jan. 10, 1943)

the paper and partially obliterates the wire and felt marks. The wetter the sheet, the greater the smoothing effect. Increased beating increases the amount of water in the sheet at the time of pressing and increases the flexibility of the fibers, both of which tend to increase the smoothing effect obtained on pressing.

Too much pressure must not be applied to the wet sheet, since this causes crushing. Crushing is the result of hydraulic pressure which is too great for the rate at which water is leaving the sheet. Crushing can be reduced by applying pressure gradually since less water is removed this way and the fibers are not so likely to be pushed apart. The sheet can stand higher and higher pressure as water is removed and the sheet becomes stronger. Graduated pressure is particularly important on heavy boards, inasmuch as the danger of crushing is greater the heavier the sheet. Pressing multicylinder boards while they are too wet leads to ply separation, as well as crushing.

Wet pressing increases the fiber bonding and increases the strength of the paper. The greater the pressure, the denser the final paper. Clark⁷⁹ found that wet pressing reduces the thickness according to the one-fifth power of the pressure and that compressed sheets regain their thickness according to the one-tenth power of the pressure remaining on them. In the case of fiberboards made from mechanically prepared pulps, there is a logarithmic relationship between the dewatering pressure and the solids content of the pressed mat, as shown in Figure VIII-1.⁸⁰ These results indicate that the same solids content is obtained at the same pressure, regardless of the amount of refining given the pulp. There is, however, a difference in the rate at which pressure can be applied to different pulps, and consequently there is a difference in the time required for equilibrium to be reached.

Commercial pulps vary in their compressibility and in their ability to recover their original shape after the pressure is removed. This difference in compressibility affects the solid fraction and strength of the final paper.⁸¹ Groundwood pulps are markedly less compressible than sulfate pulps,⁸² and groundwood pulps show the least recovery after compressive deformation, followed by sulfite pulps, and then by kraft pulps.⁸¹ Campbell⁸² found that beating has relatively little effect on the compressibility of kraft pulps,

⁷⁹ J. d'A. Clark, *Pulp Paper Mag. Canada* 44: 91-102, Convention Issue (1943)

⁸⁰ H. D. Turner, J. P. Hohf and S. L. Schwartz, *Paper Trade J.* 127, No. 9: 43-50 (Aug. 26, 1948)

⁸¹ C. O. Seborg, F. A. Simmonds and P. K. Baird, *Paper Trade J.* 109, No. 8: 83-90 (Aug. 24, 1939)

⁸² W. B. Campbell, *Pulp Paper Mag. Canada* 48, No. 3: 103-109, Convention Issue (1947)

but Baird and coworkers⁸³ found that beating produces a marked decrease in the recovery value of all pulps. Jahn and coworkers⁸⁴ found that pressures of 3,000 p.s.i. are required to overcome the stiffness of unbeaten fibers, compared with much smaller pressures required for beaten fibers. Well-cooked pulps recover less after compression than raw, shivy pulps. Re-

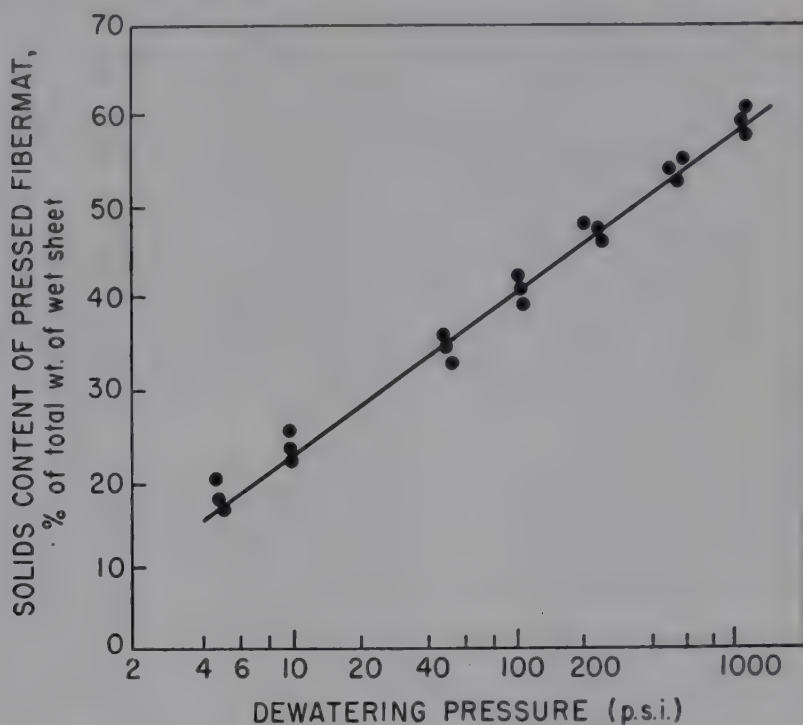


Fig. VIII-1. Relationship between dewatering pressure and solids content of wet fiberboard mats.

duced surface tension, increased temperature, high springwood content, and a high content of "fines" reduce the recovery value of the pulp.⁸⁵

Drying of Paper

The drying process consists of supplying enough heat units to the paper to evaporate most of the water remaining in the sheet after wet pressing. Sufficient heat must be supplied to raise the temperature of the water and pulp to the evaporating point, and to turn the water into vapor. Heat must also be supplied to the ventilating air so that the water vapor can be removed without condensation. Drying is a relatively expensive process, and the cost of drying is usually a large part of the cost of the final paper. If drying is not done properly, manufacturing costs will be high and the quality of the paper will be affected.

⁸³ C. O. Seborg, F. A. Simmonds and P. K. Baird, *Paper Trade J.* 109, No. 8: 83-90 (Aug. 24, 1939)

⁸⁴ A. Sedoff, C. V. Holmberg and E. C. Jahn, *Paper Trade J.* 109, No. 26: 350-357 (Dec. 28, 1939)

⁸⁵ C. O. Seborg, F. A. Simmonds and P. K. Baird, *Paper Trade J.* 109, No. 8: 83-90 (Aug. 24, 1939)

Special grades of paper may be dried by (1) loft drying, in which the wet paper is hung by hand on wooden poles in a loft or heated room and left for many hours, (2) festoon drying, in which the sheet is looped over poles and carried through a heated chamber on chain conveyors, and (3) by drying in a Barber drier, where the sheet is dried by hot air while being passed over rolls under tension. However, practically all machine-made paper is dried by passing over steam-heated metal drier rolls. This method of drying is more complicated than the above air-drying processes, because the primary source of the heat is the steam in the driers, whereas in air-drying methods, the heat is supplied by circulating air, which means that drying rate can be calculated from simple laws involving air temperature, velocity, and humidity. Furthermore, in the machine drying of light-weight papers, felts are used for holding the paper against the drying cylinders and to remove moisture from the paper mechanically. The drying of paperboard is different in that no felts are used and the water is evaporated directly from the paper surface.

The drying of heavy insulating boards (boards $\frac{1}{4}$ to 1 in. thick) offers different problems from the drying of ordinary papers. On these grades, platen driers (stationary or moving), tunnel driers, or roller driers may be used in place of the ordinary drum driers, since these heavy boards are too rigid to be wrapped about cylindrical driers. Higher temperatures are used than those employed on light-weight papers, temperatures in the neighborhood of 350 to 500° F. being common. As a consequence, care must be exercised to see that the board is not discolored by the high temperature. The temperature is generally reduced toward the end of the drying after the board has lost most of its moisture, particularly with groundwood or semichemical pulps which are easily discolored by high temperatures.

Character of Steam Used

Steam is universally used for drying because of its efficiency (1 lb. of saturated steam at 212° F. has nearly six and one-half times as much heat as 1 lb. of water at the same temperature). Steam pressures have been increasing steadily for years. At one time, steam pressures of 2 to 3 p.s.i. were used, but today, steam pressures are generally between 5 to 60 p.s.i., with some mills using pressures up to 100 p.s.i. Paperboard is generally dried at higher pressures than light-weight papers. A system of graduated pressure is generally used, the lowest pressure being used at the wet end driers and the highest pressure being used at the dry end.

The steam should be comparatively free of non-condensable gases, because these lower the efficiency. Only 5% of air by volume in the driers will reduce the drying capacity by more than 20%.⁸⁶ The drying cylinders

⁸⁶ F. L. Shonkweiler, *Pulp Paper Mag. Canada* 50, No. 11: 94-97 (Oct., 1949)

should be equipped for the quick removal of air when steam is first admitted and should also be equipped for easy removal of condensate. In one new type of drying cylinder,⁸⁷ there is a second inner cylinder providing an annular space to which steam can be admitted at several points. This causes steam to travel across the inner surface of the drier shell at very high velocity, thus preventing the formation of gas and air pockets on the inside of the drier shell.

Water in Paper Going to Driers

The amount of water in the sheet entering the drier section is important for two reasons: (1) the cost of evaporating water is a good deal more expensive (about 10 times greater) than removing water by pressing, and therefore the moisture content should be kept to a minimum to save money; (2) the quantity of water in the sheet affects the character of the finished paper. It is interesting to note what part of the water is removed at the different parts of the paper machine. For stock of 0.5% consistency, the water taken out per ton of stock at the various sections would be⁸⁶ approximately as follows: 390,000 lb. on the wire, 3,334 lb. at the presses, and 4,564 lb. in the drier section.

The moisture content of paper entering the drying section varies for different grades of paper, but it is about as follows⁸⁸ for existing machines: book and writing, 65%; board, 64%; tissues, 65 to 73%; kraft, 70%; glassine, 77 to 80%; and cylinder straw, 60%. The average paper contains approximately 65 to 75% moisture going to the driers, and this must be lowered to about 4 to 7% in the final paper.

The theoretical relationship between the amount of water in the paper when it enters the driers and the amount of steam required to dry the sheet has been given by Young⁸⁹ as follows:

Per cent water after presses	Pounds steam required to dry each pound of paper
74	3.78
72	3.42
70	3.18
68	2.80
66	2.56
64	2.33

Thus, it can be seen that increasing the moisture content of the paper from a moisture of 64% to a moisture of 74% theoretically increases the steam consumption by about 35%. Furthermore, an excessively high moisture

⁸⁷ E. A. Hodge, P. A. Jackson and P. H. Goldsmith, *Paper Trade J.* 128, No. 3: 23-27 (Jan. 20, 1949)

⁸⁸ C. Clark, *Paper Ind.* 30, No. 11: 1615-1617 (Feb., 1949)

⁸⁹ T. R. Young, *Paper Maker Intern.* No. 1946, 51-54 (1946)

content is likely to cause cockling and sticking of the sheet to the first few driers. In the commercial drying of paper, about 3.0 to 3.5 lb. of steam are generally used for each pound of paper.

The quantity of water evaporated from the paper is a necessary figure for determining drying efficiency. It can be obtained from the weight of dry paper (including dry broke) and the difference in moisture contents of the paper entering and leaving the drier section. Paper moisture can be measured by taking periodic samples of paper from the machine and running moisture tests by drying in an oven. The moisture can be measured continuously by special electrical conductivity measuring units^{90,91} which are located on the last or next to the last drying cylinder, on the calender stacks, or on an idler roll before the reel. These instruments use a balanced Wheatstone bridge in which the unknown resistance is the sheet of paper. In operation, the slide-wire resistor automatically adjusts itself to balance the system, and this balancing action moves an oscillating pointer on the control chart. The recorder must be calibrated against known samples and special calibration curves set up for each grade of paper. Multiple detector rolls permit readings to be taken across the width of the sheet.

Heat Supplied to the Drying Cylinders

Most of the heat used in drying the paper is derived from the steam introduced into the drying cylinders. The amount of heat added can be obtained from the weight of steam used and the number of heat units added per pound of steam.

The amount of steam used in drying the paper can be measured by flowmeters, or by weighing the condensate from the drying cylinders. If steam flowmeters are used, they should be carefully calibrated and allowance should be made for steam exhausted to the atmosphere during breaks. The number of heat units absorbed at the driers can be determined by subtracting the heat units in the condensate from the heat units in the original steam. This is usually expressed in heat units per pound of water evaporated obtained by dividing total heat units absorbed by the weight of water evaporated. Steam tables and a thermometer are all that is necessary to obtain this information.

Heat Supplied to the Paper

The temperature of the paper entering the driers generally varies from about 40 to 85° F., depending upon the season of the year. The paper must be heated from this temperature to the temperature of evaporation, which is normally between 180 to 200° F. Nearly all evaporation takes place below

⁹⁰ E. A. Murphy and H. A. Sholl, *Southern Pulp Paper Mfg.* 11, No. 2: 45, 48 (Feb. 15, 1948)

⁹¹ H. A. Sholl, *Tech. Assoc. Papers* 31: 375-378 (June, 1948)

212° F., and for all practical purposes, the sheet temperature may be taken as the evaporation temperature after the first two or three driers. After the paper leaves each drier roll, evaporation of moisture takes place and the sheet begins to cool. Drying is thus a series of heating and cooling periods. Sherwood and coworkers⁹² found in the drying of sulfite bond that there was a drop of 9° F. between drier rolls at the wet end, and that almost all this was due to evaporative cooling.

The amount of heat transferred to the paper can be expressed by the formula given below:

$$Q = UA\Delta T$$

where Q is the total heat transferred in B.t.u. per hour, U is the over-all coefficient of conductance in B.t.u. per hour per square foot per °F. difference, A is the area in square feet, and ΔT is temperature difference in °F. between the steam inside the drier and the temperature of the paper. This formula shows that the drying rate can be increased by increasing the coefficient of conductance, by increasing the area, or by increasing the temperature difference.

Conductance affects drying by changing the rate of heat flow from the steam to the paper. The over-all conductance is affected by (1) the rate of heat flow from the steam to the inside surface of the drier shell, (2) the rate of heat flow through the drier shell, and (3) the rate of heat flow from the drier shell to the paper. Montgomery⁹³ lists the various factors which influence conductance as follows: type of condensation (film or dropwise) in driers, steam velocity, removal of condensed steam in driers, presence of non-condensable gases or superheated steam, presence of scale on inside of driers, conductance coefficient of drier shell, condition of drier surface, condition of paper surface, moisture content of paper, tightness of draws, diameter of driers, and speed of machine. To obtain good conductance, the drier surface should be kept as clean and well polished as possible by the use of doctors and frequent conditioning, and the paper surface should be as smooth as possible. A smoothing press before the driers increases the drying rate by improving the contact between the drier surface and the paper. Tightening the draw also improves drying for the same reason. Montgomery⁹³ points out that the drying rate on a Yankee drier without predrying is five times that on the usual multidrier section because of the better contact obtained with the polished metal surface. Increasing the machine speed reduces contact between the paper and drier surface by drawing a film of air in at the nip. This air offers about 1,600 times as much

⁹² T. K. Sherwood, H. S. Gardner and R. P. Whitney, *Paper Trade J.* 106, No. 24: 327-333 (June 16, 1938)

⁹³ A. E. Montgomery, *Pulp Paper Mag. Canada* 48, No. 3: 171-174, Convention Issue (1947)

resistance to heat flow as the cast iron drier shell. The higher the moisture content of the paper, the higher the contact conductance. This means that the sheet is heated more rapidly at the wet end than the dry end of the drier section. Good drying is considered to be taking place when U equals 60 or more.

The area of heat transfer is, of course, affected by the total number of driers on the machine. The area of contact is important here, as well as with the conductance, because a sheet which makes poor contact with the drier surface is not being effectively dried at that point.

Increasing the temperature difference between the paper and the condensing steam inside the drier increases the drying rate as long as the contact conductance remains the same. One obvious method of accomplishing this is to increase the drier temperature by raising the steam pressure. Burstein⁹⁴ found that the rate of drying increases continuously with drier temperature in almost a linear relationship. Another method of increasing the temperature difference is to lower the evaporation temperature of the water in the paper by changing the quantity and relative humidity of the ventilating air.

Heat Supplied to the Ventilating Air

The ventilating air must be raised in temperature from the outdoor condition to that in the exhaust ducts. Ordinarily, about one-third of the steam requirements is used for heating the air. The heat absorbed by the air equals the total heat passing out the exhaust duct minus the total heat in the incoming air, both expressed per pound of water evaporated. The heat units in the exhaust and fresh air can be calculated from the temperature and relative humidity of the air, using suitable psychrometric charts. The heat units supplied to the air can also be determined from the weight of condensate from the air heating apparatus. The quantity of air used in ventilation can be determined from the weight of water evaporated and the quantity of water carried per pound of air.

The effectiveness of air in removing water is directly proportional to the difference between the vapor pressure of water corresponding to the sheet temperature and the partial pressure of the water in the air.⁹⁵ This difference may be increased by any one of three ways: (1) by increasing the temperature of the wet sheet, (2) by increasing the temperature of the air, or (3) by lowering the humidity of the air. The quantity of air supplied should be such, however, that the exhaust air is above a relative humidity of 80%, since exhaust air of lower humidity than this is wasteful of heat.

⁹⁴ V. C. Burstein, *Paper Trade J.* 122, No. 10: 103-110 (Mar. 7, 1946)

⁹⁵ A. E. Montgomery, *Pulp Paper Mag. Canada* 48, No. 3: 171-174, Convention Issue (1947)

The velocity of circulation of air is important, particularly after the sheet has a high temperature, because circulation brings air into contact with the sheet. In the case of pulp pads heated on a hot plate with air circulating in parallel flow over the surface, Sherwood⁹⁶ found that the rate of drying is increased by approximately 50% when the air velocity is doubled. Most machines are equipped with air blowers and fans which draw vapor from the pockets and improve the circulation.

The air temperature must not be too low, since this causes cooling of the paper by sensible heat removal, particularly at the dry end where the sheet has a low heating capacity.⁹⁷ On the other hand, the air temperature must not be too high, since this reduces flow of heat to the paper. From a theoretical standpoint, the temperature of the circulating air should be approximately the same or slightly above the sheet temperature. Montgomery⁹⁸ found the proper temperature of air on a board machine to be somewhere between 170 to 190° F.

Efficiency of Drying

The efficiency of drying is the ratio of the theoretical heat units required to evaporate a pound of water at its temperature in the sheet to the actual heat units required per pound of water evaporated. Useful figures for comparing relative drying capacities of different machines are water evaporated per square foot of drying surface and paper dried per square foot of drying surface. Another useful figure already mentioned is U , the over-all coefficient of heat transfer. Pounds of steam required per pound of paper dried is of little value for comparative purposes, because different papers have different moisture contents entering the driers. The amount of drying surface in square feet per inch of width (S/W) can be calculated as follows:

$$S/W = 0.0218(N_p D_p + N_f D_f)$$

where S is the total drying surface in square feet, W is the width in inches at reel, N_p is the number of driers, D_p is the diameter of driers in inches, N_f is the number of felt driers, and D_f is the diameter of felt driers in inches.

Stages in Drying

Water is held in the wet sheet in different ways. Part of the water is adsorbed on the cellulose crystallites, another part is held by capillary forces in the pores of the fibers, and another part is held mechanically in the pores of the sheet. In normal drying, the last, i.e., the free interfiber water held

⁹⁶ T. K. Sherwood, *Paper Trade J.* 88, No. 8: 134-136 (Feb. 21, 1929)

⁹⁷ T. K. Sherwood, H. S. Gardner and R. P. Whitney, *Paper Trade J.* 106, No. 24: 327-333 (June 16, 1938)

⁹⁸ A. E. Montgomery, *Pulp Paper Mag. Canada* 48, No. 3: 171-174, Convention Issue (1947)

mechanically in the pores, is removed first and later the capillary water is removed. Very little of the adsorbed water is removed, unless the paper is overdried.

The drying cycle for paper can be divided into three fairly distinct stages.⁹⁹ In the first stage, the rate of water removal is constant, that is, the diffusion of water from inside the sheet is sufficiently rapid to keep up with the evaporation rate. During this period of constant rate of drying, moisture is evaporated from a more or less continuous film of water on the paper surface, and the rate of moisture removal is governed by the air velocity, air temperature, humidity, and drier temperature. The temperature of the wet sheet increases quite rapidly in the very early stages, but then remains constant at the wet bulb temperature.

At some critical point, depending upon the paper and drying conditions, the rate of diffusion cannot keep up with the rate of evaporation, so that the locus of evaporation tends to move from both sides of the sheet into the interior.¹⁰⁰ This is the second stage, and from this point on, the rate of moisture removal declines linearly with a decrease in the moisture content of the paper.¹⁰¹⁻¹⁰³ Sherwood and coworkers¹⁰⁴ found that the critical point occurred on drier roll 14 on a machine making bond paper equipped with 28 drier rolls and canvas felts. In this case the critical moisture content was 70%. Increased "hydration" of the stock tends to displace the critical moisture value to a higher moisture content, thus making it necessary to remove more water below the critical point at a lower rate of removal.¹⁰⁵ This explains why drying rate decreases in the order of newsprint, printing papers, and glassine, following the decrease in the porosities of the papers.¹⁰⁶ Sub-surface evaporation is much more of a factor on heavy paperboards than on thin papers and accounts for the difficulty of drying thick boards where the heat transfer must take place through an insulating layer of partially dried fiber on the surface.¹⁰⁴ Increased sheet weight causes an upward shift of the critical moisture content. Drier felts affect drying, because part of the water must be transferred to the felt, rather than directly to the air, which retards water removal.

Later on, another critical point is reached where the moisture is re-

⁹⁹ J. G. Caulfield, L. C. Jenness and H. G. Macklem, *Paper Trade J.* 108, No. 24: 285-288 (June 15, 1939)

¹⁰⁰ D. W. McCready, *Paper Trade J.* 101, No. 13: 162-167 (Sept. 26, 1935)

¹⁰¹ T. K. Sherwood, H. S. Gardner and R. P. Whitney, *Paper Trade J.* 106, No. 24: 327-333 (June 16, 1938)

¹⁰² T. K. Sherwood, *Ind. Eng. Chem.* 22: 132-136 (1930)

¹⁰³ T. K. Sherwood, *Paper Trade J.* 88, No. 8: 134-136 (Feb. 21, 1929)

¹⁰⁴ T. K. Sherwood, H. S. Gardner and R. P. Whitney, *Paper Trade J.* 106, No. 24: 327-333 (June 16, 1938)

¹⁰⁵ V. C. Burstein, *Paper Trade J.* 122, No. 10: 103-110 (Mar. 7, 1946)

¹⁰⁶ R. E. Montgomery, *Paper Trade J.* 108, No. 8: 89-90 (Feb. 23, 1939)

moved at a very low rate and the sheet temperature starts to approach the dry bulb temperature. Changing the air velocity or the relative humidity at this stage does not appreciably speed up drying, since drying is limited by the diffusion of water molecules. A sharp rise in paper temperature in this stage denotes overdrying.

Effect of Drying on Sheet Properties

During the early stages of drying, the fibers are free to slide over one another, but as the free water is driven off, the fibers are drawn closer together and bonding begins to take place. Surface tension is primarily responsible for drawing together the fibers in this stage, but later, molecular attraction brings about the final bonding between fibers. No appreciable fiber-to-fiber bonding takes place until the moisture content is lowered below about 60%; but once the critical drying point is reached, shrinkage begins to take place and bonding begins. Lyne and Gallay^{106a} found in the case of handsheets made from sulfite pulp that shrinkage developed rapidly at about 55% solids and is mainly complete at about 80% solids. Strength development was found to begin at about the same point at which shrinkage started, i.e., 55% solids, and be complete at about 80 to 90% solids. The force responsible for shrinkage was found to be about 370 g. per 15 mm. at the maximum point (90% solids). Most of the shrinkage in commercial papers occurs rapidly over two or three drier rolls.

Some tension (draw) on the sheet is necessary to keep the sheet running and to prevent excessive cockle in the paper. This tension generally causes the sheet to expand so that it is 5 to 9% longer at the reel than it is coming off the wire, although in some cases there is apparently no expansion.¹⁰⁷ When expansion occurs, it is necessary to maintain a speed differential on the different machine sections. Of a total stretch of 6%, the stretch at each section would be approximately as follows:

Between couch and first press	2%
Between first press and second press	1%
Between third press and driers	1½%
Between driers and calenders	1%
Between calenders and reel	1½%

In watermarked papers, when it is necessary to center the watermark, allowance must be made in the location of the dandy for the expansion which occurs in the machine direction and contraction in the cross direction when the sheet is dried.

The tension maintained on the sheet during drying has an important

^{106a} L. M. Lyne and W. Gallay, *Tappi* 33, No. 9: 429-435 (Sept., 1950)

¹⁰⁷ Lecture by B. Steenberg, New York State College of Forestry (April 11, 1949)

effect on the strength of the paper. It is well known that hand-made papers dried by air in a loft under no physical restraint are much harder, have a higher bursting strength, and have a more cockled appearance than paper which is dried under tension on the paper machine. Steenberg¹⁰⁷ and Edge¹⁰⁸ report that the tensile strength of paper at the wire and couch is practically the same in both directions and stretch is slightly higher in the machine direction, but after the sheet has been subjected to the draw, machine direction tensile strength becomes greater and the stretch becomes less. In the case of handsheets, Edge was able to obtain an extremely high ratio of machine to cross direction tensile strength (4 to 1) by increasing the tension on the sheet during drying. Van den Akker¹⁰⁹ attributes this increased tensile strength resulting from drying under tension to equalization of distribution of stress among the fibers.

Increased tension during drying increases the rigidity of the paper, but reduces the "toughness" by lowering the extensibility. It is this loss in extensibility of the paper which accounts for the loss in bursting strength which usually results from drying under tension. Cottrall and Gartshore¹¹⁰ found the bursting strength of paper dried on the machine was 11 to 18% less than that of paper made from the same stock dried under no tension. This agrees roughly with the results of Sapp and Gillespie,¹¹¹ who found that kraft bag and wrapping papers lost 20% in bursting strength in passing over the driers of a commercial paper machine. Their results showed that it is possible for paper to lose up to 66% of its bursting strength if dried under maximum tension. Thus, it may be concluded that increased draw increases the tensile strength and rigidity of the paper, but reduces the toughness and bursting strength by lowering the extensibility. The results which were obtained by Sapp and Gillespie are shown in Figure VIII-2. Increased draw is desirable where stiffness is desired (e.g., writing or index papers), but is undesirable where toughness is desired (e.g., bag papers and newsprint). The effect is greater the wetter the sheet, which means that the draw at the couch is more of a factor than the draw at the last drier section.

There is relatively little cross-direction stress at the edges of the sheet compared with the cross-direction stress in the middle of the sheet. This means that paper taken from the edges of the sheet has greater stretch and

¹⁰⁸ S. R. H. Edge, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 25: 210-215 (1944); 26: 425-431 (1945)

¹⁰⁹ J. A. Van den Akker, *Tappi* 33, No. 8: 398-402 (Aug., 1950)

¹¹⁰ L. G. Cottrall and J. L. Gartshore, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* 24: 261-307 (Dec., 1943)

¹¹¹ J. E. Sapp and W. F. Gillespie, *Paper Trade J.* 124, No. 9: 120-122 (Feb. 27, 1947)

greater "flow" than paper taken from the middle of the sheet. For this reason, it has been suggested that papers requiring stretch or toughness, i.e., bag papers, be made by slitting the wet sheet and drying in three or more separate strips in order to take advantage of the increased stretch at the edges of the paper. Excessive cross-direction shrinkage at the edges of the sheet during drying results in a series of raised ribs in the machine direction, a condition known as "grainy edges." Grainy edges may occur at each edge of paper which is slit into several webs as described above.

The machine direction tension built into the paper by the draw reduces the expansion of the finished paper in this direction when wet with water. On the other hand, the lack of tension in the cross direction permits appre-

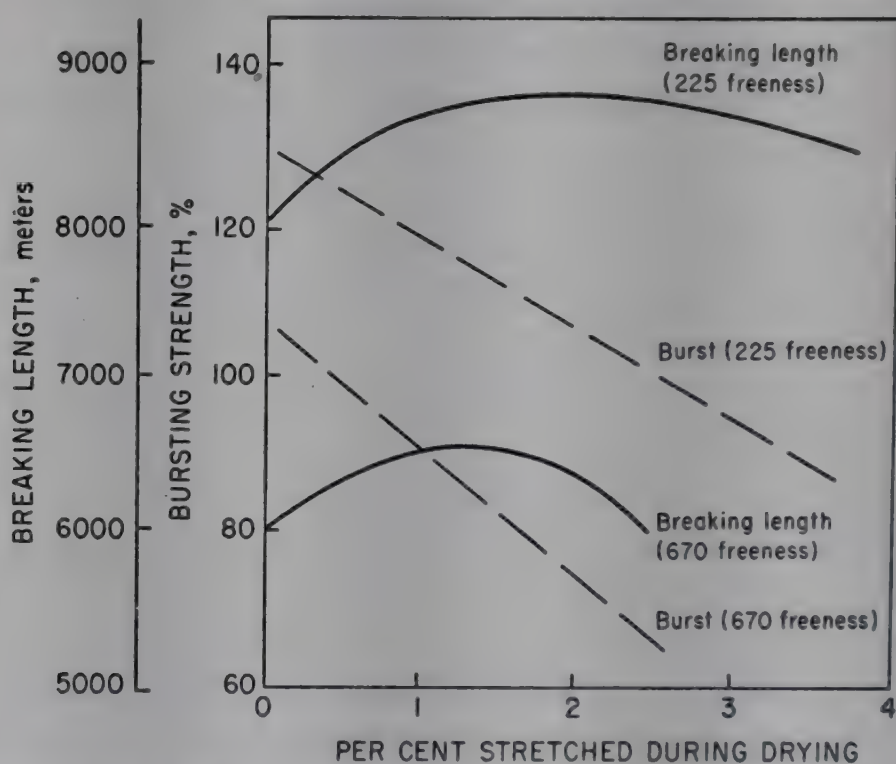


Fig. VIII-2. Effect of drying tension on bursting strength and tensile strength at freeness 225 and 670.

ciable expansion in this direction when the sheet is wetted. Hand-made papers which are dried under no tension show more dimensional change on remoistening than machine-dried paper.

In the manufacture of machine-glazed papers, using a Yankee drier, maximum strength is sacrificed to better finish by drying the sheet in contact with a highly polished metal drier roll from 9 to 15 ft. in diameter. Because the sheet is restrained from further contraction after coming into contact with the drying cylinder, it loses a considerable part of its potential strength. The advantage of this method of drying lies in the fact that the wet sheet takes on a reproduction of the highly polished drier surface so that the final paper has a highly glazed surface. A high glaze will not be

obtained if the surface of the drier loses its polish, or if the sheet is too dry when first brought into contact with the drier surface.

The paper should be raised in temperature slowly at the wet end, since this reduces picking, blistering, blowing (in the case of multicylinder boards), case hardening, and inhibits cockling and curling. Graduated drying is desired from the standpoint of improved sizing. The paper should never be overdried, since this causes oxidation of the cellulose, resulting in brittleness and reduced strength. Rich¹¹² gives the following figures to illustrate the drop in viscosity which may take place on drying..

Grade	Viscosity of pulp		Loss of viscosity on drying
	Before drying	After drying	
Plain bond	169	158	6.5%
Tub-sized bond	137	102	25.5%
Waterleaf	58	57	1.7%

Overdrying reduces the strength by lowering the moisture content of the sheet below the optimum point. Brecht¹¹³ reports that, in general, paper is reduced in strength by drying, as evidenced by the fact that paper taken off the dry end of the paper machine has a lower tensile strength than the same paper on the wire when the former is rewetted to the same moisture content as the latter. Lyne and Gallay^{106a} believe that the loss in bursting and tensile strength resulting from drying occurs in the early stages of the drying process when the fibers are heated in the presence of a considerable excess of water. This, they believe, results in a deswelling of the fibers and a loss in their potential bonding qualities similar to the effect (previously pointed out) which is produced when fibers are heated in water suspension.

Separate steam headers are generally used in the different sections so that drying can be controlled separately in each section. Control is achieved (in the Stamm control system) by use of a small pilot cylinder equipped with a separate steam supply which measures the drying load by the amount of steam condensed in it. Variation in the amount of water condensed in the pilot cylinder controls either the pressure of the steam admitted or the amount of steam admitted to the various sections.

Effect of Machine Speed

Each particular machine has an optimum operating speed which depends upon the grade of paper, basis weight of paper, and the mechanical condition of the machine. Machine speed is important not only from a

¹¹² E. D. Rich, *Paper Trade J.* 112, No. 6: 63-68 (Feb. 6, 1941)

¹¹³ W. Brecht, *Das Papier* 3, 189-192 (1949), through *Paper Ind.* 31, No. 4: 1118 (Dec., 1949)

production standpoint but also for its effect on the quality of the paper. The optimum operating speed is the point at which the many variables average out to the most favorable condition. Any variation in machine speed brings about corresponding changes in the amount of wet pressing or drying of the paper unless compensating adjustments are made. The ranges of machine speeds generally employed for the manufacture of different grades of paper using machines especially built for that grade are shown in Table III.¹¹⁴ There is, of course, considerable variation from mill to mill and many mills operate at much lower speeds than those indicated in the table. As machine speeds have approached 2,000 f.p.m., it has been necessary to redesign paper machines.

TABLE III
MACHINE SPEEDS FOR DIFFERENT GRADES OF PAPER

Type of paper	Speed of machine, f.p.m.
Greaseproof	450- 550
Sulfite papers	900-1200
Groundwood papers (including machine-coated)	900-1200
Newsprint	1400-1600
Kraft container board	1200-1500
Kraft paper	1400-1600
Creped tissue	1500-2400

Calendering and Supercalendering

After the sheet is dried, it is passed through a stack of heavy metal rolls where it is calendered under high pressure. The paper is then reeled, after which it is passed through slitters and rewind. The paper is then sent to the finishing department where it may be cut, trimmed, sorted, embossed, plated, supercalendered, inspected, sealed, labeled, and packaged.

Certain grades of paper are passed through a two-roll stack, called a breaker stack, about one-third of the way along the drier section. This smoothes the paper while it still contains a high percentage of moisture and is most susceptible to calendering. As a result, the paper is appreciably increased in density, bursting strength, and finish. The finish obtained on a breaker stack is more permanent than that obtained on calendering.

Machine Calendering

Machine calenders are made up of a number of all-metal rolls, usually two stacks of rolls containing eight or nine rolls each. The bottom roll of the calender roll stack is generally the only roll that is driven, the other rolls being turned by surface friction. Calenders equipped with anti-friction

¹¹⁴ J. E. Goodwillie, *Tappi* 33, No. 5: 99A-102A (May, 1950)

bearings produce as high a finish as those equipped with regular bearings, indicating that roll slippage plays little or no part in the action of machine calenders.¹¹⁵ Baird and coworkers¹¹⁶ found that the total increase in speed and roll slip is only about 1.4% and that this is caused by a stretching or extrusion of the paper. The important factor in machine calendering is the pressure used. This varies from very low pressures on low-finish papers to very high pressures on special papers. Pressures equivalent to 10,000 to 20,000 p.s.i. are mentioned by Strachan.¹¹⁷ The effects of calendering increase with roll pressure. However, Brecht¹¹⁸ has pointed out that they do not increase in direct proportion to the pressure applied, because the area of contact increases with an increase in applied pressure, thus giving proportionately less increase in pressure per unit of contact area.

Calender rolls tend to sag, and hence must be crowned. Crowning generally varies from 0.001 to 0.002 in. for the top rolls to 0.009 to 0.055 in. for the bottom rolls. If the top or bottom rolls are incorrectly crowned, the nip pressures in the stack will be non-uniform across the face, and no amount of crowning in the intermediate rolls will correct it.¹¹⁹ Gough¹¹⁹ points out that slip results between any pair of rolls which do not have crowns proportional to their diameters, and since the slip is different across the face of the rolls (being greatest at the ends and centers of the roll and zero at the quarter points), a non-uniform finish is produced on the paper. He suggests the following crowns for a 10-roll supercalender 157 in. in width: top roll, 0.0824 in.; intermediate rolls, zero; bottom roll, 0.0524 in. These crowns are based upon the theoretical vertical loading which is necessary to provide uniform nip pressures across the face.

Calendering is not always even across the width of the paper because of differences in the thickness of the paper. The uneven pressure resulting from the high and the low spots tends to form hard and soft spots in the calendered paper. Localized pressure can be obtained in calendering, if desired, by placing a small piece of felt beneath the doctor blade to generate heat and cause expansion of the calender roll at that point. On the other hand, if there is too much pressure at a particular spot, the roll may be cooled by concentrating a jet of cool air on this point.

The principal objective in calendering is to increase the smoothness and finish of the paper. Calendering also reduces the thickness and increases the density, the thickness after calendering being inversely propor-

¹¹⁵ G. A. Schoonkind, *Paper Ind.* 28, No. 10: 1443-1446 (Jan., 1947)

¹¹⁶ G. E. Mackin, E. L. Keller and P. K. Baird, *Paper Trade J.* 113, No. 5: 53-61 (July 31, 1941)

¹¹⁷ J. Strachan, *Proc. Tech. Sec., Paper Makers' Assoc. Gt. Britain Ireland* (March, 1926)

¹¹⁸ W. Brecht, *Paper-Maker* 97, No. 4: TS41-52 (Apr., 1939)

¹¹⁹ J. B. Gough, *Paper Trade J.* 125, No. 19: 213-218 (Nov. 7, 1947)

tional and the solid fraction being directly proportional to the lineal pressure of calendering.¹²⁰ Calendering makes the paper more uniform in thickness, but this uniformity in thickness is obtained at the expense of uniformity in density. The opacity of the paper is reduced because the fibers are pressed closer together, thereby destroying air-fiber interfaces. Calendered paper has a greater area than uncalendered paper. The paper is expanded in both the machine and cross directions, but mostly in the cross direction. As a rule, calendering increases the tensile strength slightly, although too drastic calendering will reduce tensile strength. The greatest improvement in tensile strength occurs when the paper is relatively moist at the time of calendering. Bursting strength is not greatly affected by calendering, but tearing strength and folding endurance decrease upon calendering, the greatest loss occurring at the higher calendering pressures.¹²⁰ According to Steenberg,¹²¹ calendering tends to break down the structure of paper, thereby increasing its viscous flow properties. Porosity is reduced and oil absorbency is reduced, particularly when the paper is calendered at high moisture content. Baird and coworkers¹²⁰ found that air resistance increases regularly with increasing roll pressure, but that oil resistance increases irregularly. Simmons and coworkers¹²² found in the calendering of newsprint that smoothness increases regularly with each nip, but that oil resistance is not appreciably increased after the first nip. Calendering tends to reduce the sizing.

The effects of calendering increase with the moisture content of the paper, because increased moisture makes the fibers more plastic. Papers calendered at high moisture content generally show greater strength, density, gloss and oil resistance, but lower brightness and opacity than papers calendered at low moisture content. Papers of very high moisture content must not be calendered excessively, since this leads to blackening, a condition of transparency resulting from fibers being crushed in contact with each other.¹²³ These areas reflect less light and hence appear dark. Paper generally has a moisture content of 6.0 to 8.0% on going to the calenders. Lower moisture than this tends to produce curling, whereas higher moisture causes wrinkling and blackening. The effect of moisture in the range of 2.4 to 3.4% in the calendering is shown in Table IV. These are results obtained on an experimental calender at the Forest Products Laboratory.¹²⁴

¹²⁰ G. E. Mackin, E. L. Keller and P. K. Baird, *Paper Trade J.* 113, No. 5: 53-61 (July 31, 1941)

¹²¹ B. Steenberg, *Pulp Paper Mag. Canada* 50, No. 3: 207-214, 220, Convention Issue (1949)

¹²² B. L. Wehmhoff, R. H. Simmons and D. H. Boyce, *Paper Trade J.* 96, No. 4: 48-52 (Jan. 26, 1933)

¹²³ C. G. Albert, *Paper Trade J.* 105, No. 6: 89-93 (Aug. 5, 1937)

¹²⁴ G. E. Mackin, E. L. Keller and P. K. Baird, *Paper Trade J.* 113, No. 5: 53-61 (July 31, 1941)

Blackening was obtained in these experiments at a moisture content of 4%, which is lower than the moisture at which blackening occurs in commercial practice. In order to increase the moisture content of the paper at the time of calendering, the paper may be passed over a water-cooled sweat roll just before entering the stack so that moisture is condensed from the atmosphere onto the surface of the paper. In other cases, water is applied directly to the paper surface by means of a water box on one or more calender rolls. Water boxes can be used only with heavy papers where the excess water is absorbed by the paper. If starch or similar material is used in the water box, the operation is called calender sizing.

TABLE IV
EFFECT OF MOISTURE ON CALENDERING

Moisture content, %	Pressure, lb./lin. in.	Burst, pt./lb.	Tear, pt./lb.	Tensile, p.s.i.	Gloss, %	Solid fraction ratio	Porosity, sec.
2.4	Uncalendered	0.19	0.76	1960	20	0.42	53
4.3	Uncalendered	0.21	0.81	2100	20	0.43	62
2.4	2040	0.20	0.72	2650	31	0.55	108
4.3	2040	0.19	0.67	2945	50	0.64	149
2.4	2860	0.20	0.70	2235	35	0.58	133
4.3	2860	0.19	0.62	3290	53	0.67	182

Brecht¹²⁵ reports that papers made on the paper machine with a high moisture content calender much more readily than papers of the same moisture content containing water added in a remoistening operation. This is apparently due to a partial irreversibility in the imbibition of water by the cellulose. However, adding moisture after the paper has once been dried results in less blackening on calendering compared to the results obtained when paper is simply dried down to the same moisture content.¹²⁶ The remoistening of paper prior to machine calendering is intended merely to soften up the surface fibers, and not the fibers in the interior of the paper.

The temperature of calendering is quite important, because heat makes the paper more pliable and more easily ironed out, just as heat makes clothes easier to iron. In the days of hand-made papers when individual sheets were finished, it was customary to heat the paper to 90 to 110° F. before putting it through the sheet calender. In machine calendering, the paper generally has a temperature from 140 to 200° F., due to the heat picked up in drying. Furthermore, calendering itself develops some heat. In calender sizing heavy papers with starch, it may be necessary to heat the paper still further to drive the size into the board. This is done by steam-

¹²⁵ W. Brecht, *Paper-Maker* 97, No. 4: TS41-52 (Apr., 1939)

¹²⁶ R. H. McKee and J. S. G. Shotwell, *Paper Trade J.* 97, No. 6: 61-70 (Aug. 10, 1933)

heating one or more of the metal rolls. On the other hand, one or more rolls may be cooled by circulating cold water if it is desirable to keep the calender size on the surface, or if the paper tends to dry out too much on the surface.

The ease of calendering depends to a large extent upon the type of furnish. Highly beaten stocks tend to calender more readily than lightly beaten stocks, but tend to blacken more. Brecht¹²⁷ points out that papers of low density will take a better finish than papers of high density, because they will stand much greater pressures without blackening. Fillers, particularly clay, improve the smoothness on calendering. At least part of the effectiveness of filler clay is due to the effect which it has on the moisture content. Rowland and Allison¹²⁸ found a correlation to exist between the hydration properties of the clay and the finishing characteristics of the filled paper. The more hydrous the clay, the greater the calendering effect and, in fact, highly hydrous clays tend to cause blackening. It is now generally believed that the blackening obtained with clay-filled sheets is related to the plate-like structure of the clay particles, since sheets filled with pigments of cubic structure such as calcium carbonate do not blacken on calendering.¹²⁹ Breaks in the paper web often occur at the calenders. These are generally due to raised spots in the paper which cut the paper under the high pressure.

The amount of calendering can be varied by changing the number of nips through which the paper is passed. Certain low-finished papers may be passed through only one to two nips, whereas highly finished folding box-board may be passed through all the nips on three stacks of seven to nine rolls each. Table V gives the calendering conditions normally employed

TABLE V

CALENDERING CONDITIONS USED FOR DIFFERENT FINISHES ON PAPERBOARD

Finish number	Calendering conditions
1	2 to 4 nips—very little pressure—no water boxes
2	About 10 nips—medium pressure—no water boxes
3	About 10 nips—heavy pressure—2 water boxes on side
4	About 15 nips—very heavy pressure—2 water boxes per side—steam-heated rolls

in obtaining different finishes on paperboard. The surface of the rolls are very important. If too rough, the rolls are likely to cause blackening before a satisfactory finish is obtained.¹³⁰

¹²⁷ W. Brecht, *Paper-Maker* 97, No. 4: TS41-52 (Apr., 1939)

¹²⁸ B. W. Rowland and H. J. Allison, Jr., *Paper Trade J.* 111, No. 3: 25-28 (July 18, 1940)

¹²⁹ M. N. Davis, *Paper Trade J.* 111, No. 14: 184-188 (Oct. 3, 1940)

¹³⁰ J. B. Gough, *Paper Trade J.* 125, No. 19: 213-218 (Nov. 7, 1947)

Supercalendering

Supercalenders are made up of alternate metal rolls and paper- or cloth-filled rolls. The paper is passed between these rolls under very heavy loading. The fiber rolls provide a resilient surface in contact with the paper. As the fiber rolls enter the nip during calendering, they are distorted so that their diameter is reduced, thus causing a slowing-up of the fiber roll surface until a minimum is obtained at the center of the nip. As the fiber rolls leave the center of the nip, they expand to their original size, and their surface speed increases. This produces a creep in the fiber rolls in a direction opposite to the direction of rotation. This results in a polishing action on the paper next to the metal roll,¹³¹ since there is no appreciable displacement of the web relative to the fiber roll because of the high coefficient of friction between the paper and fiber roll.^{134,135} Schacht and Kirchner¹³⁶ found an over-all speed differential of only 0.3 to 0.4% between the top and bottom rolls of a nine-roll supercalender, which was probably due to elongation or extrusion of the paper.¹³⁷ If two fiber rolls are run together near the center of the stack, the sides of the sheet contacting the metal polishing rolls are reversed. If there is no reversal point, the paper must be run through the stack twice in order to finish both sides.

Supercalendering is done on high-finish book papers, glassine, roto-gravure, and other grades of coated paper. Book-grade supercalenders generally have seven to fourteen rolls of 40 to over 200 in. in width, maximum nip pressure of 1,000 to 2,000 p.l.i., and speeds up to 3,000 f.p.m.¹³⁸ Most grades are calendered at 100 to 400 p.s.i., although working pressures up to 600 to 800 p.s.i. are used. Glassine types generally have sixteen to twenty rolls of 40 to 96 in. in width, maximum nip pressure of 2,000 to 3,500 p.l.i., and speeds up to 1,500 f.p.m.¹³⁹ Pressure is applied by the weight of the rolls and also by means of a direct pressure hydraulic system or by a pneumatic system. Of a total operating pressure of 1,150 lb. per linear inch on the bottom roll, Riley¹⁴⁰ estimates that about 400 lb. is applied pressure from the hydraulic or pneumatic system.

The paper undergoes a stronger polishing action in each succeeding nip. The smaller the metal rolls in the stack, the greater the polishing effect, because small metal rolls cause greater deflection of the fiber rolls.

¹³¹ E. E. Thomas, *Paper Trade J.* 122, No. 22: 235-237 (May 30, 1946)

¹³⁴ G. A. Schoonkind, *Paper Ind.* 28, No. 10: 1443-1446 (Jan., 1947)

¹³⁵ R. Dittmar, *Wochbl. Papierfabr.* 69, No. 20: 425-428 (May 14, 1938)

¹³⁶ W. Schacht and E. Kirchner, *World's Paper Trade Rev.* 56, No. 7: 289-290 (Aug. 18, 1941)

¹³⁷ G. E. Mackin, E. L. Keller and P. K. Baird, *Paper Trade J.* 113, No. 5: 53-61 (July 31, 1941)

¹³⁸ E. E. Thomas, *Paper Trade J.* 129, No. 6: 41-43 (Aug. 11, 1949)

¹³⁹ E. E. Thomas, *Paper Trade J.* 129, No. 6: 41-43 (Aug. 11, 1949)

¹⁴⁰ R. W. Riley, *Pulp Paper Mag. Canada* 50, No. 7: 109-110 (June, 1949)

The resiliency of the fiber rolls is an important factor, since the softer the roll, the greater the surface distortion and the greater the creep. On the other hand, if increased pressure is desired, harder rolls must be used. Increasing the stack pressure is not effective in increasing nip pressure, since the nip only grows wider with increased stack pressure and actual pressure in pounds per square inch remains essentially the same. As a rule, paper-filled rolls produce a higher finish than cotton-filled rolls. On the other hand, cotton-filled rolls do not compact the sheet as much as paper-filled rolls, because they are more plastic and reach the low spots in the paper at lower pressure. Hence, cotton-filled rolls are preferred for papers where a combination of high finish and high bulk is desired, e.g., coated papers.

When starting a supercalender equipped with new rolls, it is necessary to allow a breaking-in period ranging from about 8 hours for hard paper-filled rolls to about 15 to 20 hours for cotton or soft-paper-filled rolls. During this breaking-in period, pressure is applied gradually and the rolls are wetted at intervals with a sponge to develop a high polish. Before paper is run on the stack, the rolls should be inspected to see that they are uniform in diameter, are free of markings, have a uniformly smooth surface, and that they are raised to the standard operating temperature. Doctor blades are used, generally on the top and bottom rolls, to keep the rolls clean and in good condition, and to prevent damage to the filled rolls which might result from paper wrapping around the stack during a break. The doctor blades may be oscillated to avoid marking of the rolls.

Supercalendering produces a much higher finish than can be obtained on machine calenders. The gloss is higher because of the greater polishing effect. Gloss is obtained mainly by friction, whereas smoothness is produced mainly by pressure. Thus, the high pressure and low friction on machine calenders produce a smooth paper, but one of relatively low gloss. Supercalenders produce not only a higher finish, but also a more uniform finish because of the resilient backing provided by the fiber rolls.

Printing papers are generally supercalendered at 150 to 180° F. Heat is developed during calendering, depending upon the speed and pressure of calendering and the softness of the fiber rolls. Steam may be used in one or more of the metal rolls if more heat is desired. However, too high a temperature has an adverse effect on the fiber rolls, and for some papers, cooling water must be used in one or more of the metal rolls. The paper is generally steamed before supercalendering by passing the paper through steam showers which apply unsuperheated steam to the paper.

Glassine papers are generally dampened to 20 to 30% moisture in a special moistening machine and then aged for one to six hours before supercalendering to allow the moisture to distribute itself throughout the paper. A uniform distribution of moisture is desired in the case of glassine

in order to obtain uniform compacting of the paper. This is different from most papers where only a surface finish is desired. Plasticizer (e.g., glycerine, corn syrup, or inert sugar) is generally added with the dampening water. The metal rolls in the stack are generally heated with high-pressure steam to increase the temperature of calendering. Supercalendered paper generally contains 4 to 8% moisture.

The fiber rolls in a supercalender must be kept in good shape. Imperfections in the fiber rolls can sometimes be removed by running the stack without any paper or by sanding, but if this fails, the rolls must be reground. Pits should be completely removed in regrinding, since otherwise they will reappear after the rolls are put back into service. The supercalendering and other special finishing of coated papers are discussed in Chapter XVIII.

Plating and Embossing

Plating is done on special grades of paper where special effects are desired. In plating, sheets of paper are placed between two layers of material whose surface it is desired to reproduce on the paper. Metal plates are added for rigidity, and when a "book" is obtained, the assembly is run between heavy rollers so that the paper takes on the impression of the plating material. Linen cloth is the most common material used, but other finishes are obtained by using cardboard, burlap, or rippled paper.

Embossing is done by running the paper between two rolls, one of which has a raised design and the other is hollowed out in the identical pattern. When the paper is passed between the two rolls under pressure, the design is embossed into the paper. Both rolls may be metal rolls, or one metal roll and one paper- or cotton-filled roll can be used. It is very important that the paper have the correct moisture content. If the moisture content is too low, the paper will not be plastic enough to take the design, whereas if the moisture is too high, the design will tend to come out of the paper. Some of the grades of paper commonly embossed are napkins, book covers, wallpaper, table covers, and photo mountings.

FILLING AND LOADING

The process of adding mineral matter to paper stock prior to the formation of the sheet is extremely old, having been practiced in the ancient days of papermaking. At first it was considered poor practice, and any paper containing an appreciable amount of mineral matter was considered to be adulterated. Later, as the uses for paper became greatly expanded, many papers were developed in which fillers were considered to be highly beneficial. Today, fillers such as clay, calcium sulfate, titanium dioxide, barium sulfate, talc, and others are commonly used as an integral part of certain grades of paper. The process is called "filling" or "loading" and cannot be considered as adulteration of the paper, since the presence of the pigment improves the properties of the paper when used in the proper proportion. In fact, it would be almost impossible to make certain grades of paper without the use of fillers. Fillers are highly desirable in printing papers where they increase the opacity and improve the surface and printability of the sheet. Fillers also improve the appearance and absorbency of paper, as well as increasing the density.

Commercial Use of Fillers

The subject of filling is a highly interesting one to the paper chemist. There are a large number of fillers which are available, and these range from cheap, low-grade clays to the expensive titanium pigments. From a practical standpoint, both have their place in the paper industry. In addition to the large choice of pigments, the paper chemist is confronted with the problem of choosing the best method of applying fillers. This section is concerned with the practical side of these questions.

Types of Fillers Used

The principal fillers used are clay, talc (agalite and asbestine), calcium carbonate, titanium dioxide, zinc sulfide, calcium sulfate (pearl hardening and gypsum), diatomaceous silica, calcium sulfite, and blanc fixe. Colored pigments are sometimes used, but these are discussed in the chapter on coloring (Ch. XIII). Of all these, clay and calcium carbonate are by far the most widely used.

Pigments must meet certain requirements to be suitable for filling.

They should have a high degree of whiteness, a high index of refraction, small particle size, low solubility in water, and low specific gravity. Moreover, it is desirable that the pigment be chemically inert so that it will not result in unfavorable reactions with the other constituents of the sheet. Furthermore, unless the pigment has very unusual properties, it must be cheap.

Clay meets most of the above requirements (except high refractive index), and hence is admirably suited for filling. This accounts for the large quantities of clay which are consumed in the manufacture of newsprint, book, and printing papers. In general, the more expensive water-washed clays give the best results, but air-floated clays are frequently used because of their lower cost. Titanium and zinc pigments are too expensive for general use, but they have the ability to impart a high degree of whiteness and opacity in low percentages, and consequently are often used in the higher grades of book, offset, and writing papers. Up to 9% titanium dioxide may be used in airmail papers, and up to 15% in Bible paper and paper for laminated plastics.

Some pigments have the disadvantage of being too reactive, for example, calcium carbonate, which tends to react with alum and rosin size, and zinc sulfide, which reacts with alum. Zinc oxide is not suitable at all because of its reactivity with alum. Pearl hardening has the disadvantage of imparting low opacity, although it does produce a high whiteness. Barium pigments have a very high specific gravity and are very poorly retained, but barium sulfate is sometimes used because it imparts an exceptionally high brilliance to the sheet. Calcium sulfate and titanium-calcium pigment have the disadvantage of high solubility.

Talc, a hydrated magnesium silicate with the approximate formula of $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$, is sometimes used for the characteristic soapy and greasy feel which it imparts to paper, and also because it improves sheet formation. Talc is available in both a fibrous and a non-fibrous form. Talcs frequently contain relatively coarse material, but air-separated grades are available which are free of large particles. The calcium content varies greatly, being highest in the New York State deposits, and somewhat less in the Vermont and California deposits. High calcium talcs are the whitest, but the calcium is harmful to sizing and certain dyestuffs. For this reason, it is best to add talcs after the beater has been completely furnished.

Amount of Filler Used

The amount of pigment used in filling varies from 2 to 40% on the weight of the fiber, 4 to 15% being a good average. Many different grades of paper are customarily made with fillers, and some of these grades, to-

gether with the amount and type of filler generally used, are given in Table I.

TABLE I

TYPE AND AMOUNT OF FILLER USED IN DIFFERENT GRADES OF PAPER

Paper grade	Type of filler	Amount of filler added, %
Bond and writing	High-opacity pigment plus clay	1- 6
Book	Clay plus high-opacity pigment	5-40
Offset paper	Clay plus high-opacity pigment	0-10
Bible paper	Clay and chalk plus high-opacity pigment	20-30
Cigarette paper	Fine chalk	35-40
Mimeograph	Clay and diatomaceous silica plus high-opacity pigment	20-25
Envelope	Talc or clay plus high-opacity pigment	10-20
Newsprint	Clay or calcium carbonate	2- 6

Methods of Adding Fillers

Ordinarily, the method of adding filler is not very complicated. In many cases, the pigment is added dry to the stock in which it is dispersed by the action of the beater. When this method is used, all the grit and foreign matter are added with the pigment. Consequently, it is considered better practice to disperse the pigment in water first and then pass the slurry through a screen before adding to the stock.

Clay is usually mixed in water before adding to the stock, and some papermakers prefer to mix in a little rosin size, believing that the rosin added in this way aids retention. Clay disperses better in hot or warm water than in cold. In some cases, dispersing agents may be used to improve the dispersion, and according to Hauser,¹ dispersing agents are desirable with clay because the beater cannot be depended upon for dispersing the clay to a uniform particle size. Furthermore, the use of dispersing agents with clay makes it possible to prepare concentrated slurries up to 60 to 70% solids, thereby facilitating handling problems.

One unusual method of filling calls for the reaction of two appropriate chemicals in the beater to form pigment directly in the stock. Calcium carbonate has been added in this way by first adding a solution of calcium chloride to the stock, followed by a solution of sodium carbonate, but this is an old technique and is seldom practiced anymore. In one mill making newsprint,² calcium carbonate is produced by passing scrubbed flue gas into a lime slurry and, after screening through a 100-mesh screen, adding the slurry directly to the paper machine furnish.

The ordinary procedure in filling is to add the filler early in the beating

¹ E. A. Hauser, *Paper Trade J.* 105, No. 7: 111-113 (Aug. 12, 1937)

² H. R. Davidson, *Pulp Paper Mag. Canada* 46, No. 3: 205-211, Sixth Wartime Issue (1945)

cycle in order to insure thorough mixing with the stock and complete dispersion of the pigment particles. However, when using calcium carbonate, some mills prefer to add the filler just before sheet formation (for instance, at the fan pump) in order to reduce the time of contact and inhibit the reaction with the rosin size and alum. There are a number of patented processes pertaining to special methods of adding calcium carbonate.³ When using waste paper containing calcium carbonate as, for example, papers coated with calcium carbonate, certain precautions may be necessary, since large amounts of this pigment are likely to cause foaming, loss in sizing, change in shade, or poor formation. If the amount of carbonate-containing waste paper is small in relation to the total fibrous furnish, probably no trouble will be encountered, although it may be necessary to add slightly more alum to obtain the desired pH.

The Fair process consists of adding filler to the wet web of paper on the paper machine wire.⁴ A dilute pigment slurry is sprayed on a curved metal shield covered with corrugated rubber sheeting and the pigment is transferred to the top surface of the wet sheet by means of a soft rubber lip which makes very light contact with the stock-water film. The advantage of this process is that it eliminates the loss of pigment which ordinarily occurs in the early stages of sheet formation. The point of addition to the paper can be varied, depending upon the weight and density of the sheet. For light porous papers, the filler should be added close to the suction boxes in order to prevent too much being sucked out the other side of the sheet. For heavy or dense papers, the filler should be applied closer to the head-box. Retention figures⁵ on calcium carbonate in a newsprint furnish comparing the Fair process with addition at the fan pump are as follows: added at Fair clay pans, 88% retention; added at fan pump, 72% retention. Retention of clay is generally in the neighborhood of 80 to 85% and can be increased to over 87% by treatment of the clay slurry in the storage tank with alum. This improves retention by coagulating the extremely fine clay particles.⁶ In addition to high retention of pigment, there are operational advantages to be gained by keeping the pigment out of the mill system.

Effects of Filling

Fillers are added to paper to improve both the optical and the physical properties. The principal object in filling is to increase the opacity and brightness of the paper, and the next most important object is to improve the smoothness, finish, and printability of the sheet, particularly after calen-

³ Patents held by the Raffold Corporation

⁴ A. E. H. Fair, U. S. 2,062,563 (Dec. 1, 1936)

⁵ H. R. Davidson, *Pulp Paper Mag. Canada* 46, No. 3: 205-211, Sixth Wartime Issue (1945)

⁶ R. E. Hayes, *Pulp Paper Mag. Canada* 37: 102-104, Convention Issue (1936)

dering. The printability of the paper is improved because clay particles are more readily wetted by ink than are the fibers and because the clay produces more and finer capillaries in the sheet.

Other characteristics imparted to the paper through loading are increased weight, improved softness, and improved absorption properties. There may be other special reasons for adding fillers as, for example, the use of calcium carbonate in cigarette papers to regulate the rate of combustion, and the use of carbon as a conducting agent in electrical conducting papers.

The use of high percentages of filler in paper results in certain undesirable effects, chief of which are a decrease in the strength and in sizing. Ordinarily, sizing is not seriously affected until 10 to 15% filler is added, but higher percentages than this may cause considerable reduction in sizing, and even lesser amounts of the alkaline pigments, such as calcium carbonate, are harmful. Fillers also decrease the bulk, since the pigment is heavier than the fiber and consequently increases the weight more than the thickness of the sheet. An undesirable effect sometimes noticed on heavily filled sheets is a "dusting" of filler out of the sheet, particularly during calendering.

Diatomaceous silica is used in the beaters for dispersing pitch. It also improves the drainage rate on the paper machine wire and, in some cases, increases the rate of moisture release on the driers.^{7,8} It tends to lower the density of the paper.⁹

The most reliable method of testing an unknown pigment is by comparing with a known pigment in handsheets. In this way, it is possible to obtain information on the opacifying properties, brightness, and surface characteristics which the pigment imparts to the paper. Some indication of the retention of pigments can be obtained, but in general, laboratory retention studies do not correlate well with results obtained on commercial paper machines. Routine tests on the pigment itself, i.e., tests such as color, presence of grit, presence of foreign matter, specific gravity, particle size, and index of refraction, give useful information, but are not so informative as are laboratory tests on handsheets. The abrasiveness of paper fillers can be determined in a special tester¹⁰ which measures the loss in weight of a piece of standard Fourdrinier wire caused by rubbing a perforated block back and forth over the wire while a slurry of the material being tested is pumped through the block and wire.¹¹

⁷ W. H. Hall, *Paper Trade J.* 115, No. 14: 181-183 (Oct. 1, 1942)

⁸ R. G. Quinn and C. J. O'Neil, *Paper Trade J.* 118, No. 9: 12, 14, 16 (Mar. 2, 1944)

⁹ W. R. Monette, *Paper Trade J.* 118, No. 19: 161-162 (May 11, 1944)

¹⁰ Abrasion Tester, Manufactured by the Valley Iron Works, Appleton, Wisconsin

¹¹ J. D. MacDonald and J. W. Kenney, *Tappi* 32, No. 11: 516-519 (Nov., 1949)

Effect on Opacity

White fillers greatly increase the opacity of the average paper, and at the same time they also increase the brightness. The opacifying and brightening effects are determined by the amount of light scattered, reflected, and absorbed by the pigment. It is possible to increase the opacity by the use of dyestuffs and colored pigments, but this lowers the brightness, because the opacity obtained is mainly due to the absorption of light. White fillers, on the other hand, increase the brightness as well as the opacity because they function mainly by increasing the refraction and reflection of light. Exceptionally high opacity can be obtained at fairly high brightness levels by using dyestuffs in combination with a white pigment. In this case, the opacity is due to a combination of the light-absorbing powers of the dyestuff and the high refracting powers of the white pigment. Dull or colored pigments have a greater opacifying power than white pigments because of their greater light absorption powers, but they, of course, do not produce a white sheet of paper.

The opacity of paper depends upon the thickness of the paper, the number of individual particles making up the sheet, and the refractive indices of these particles. Groundwood has a higher opacity than bleached sulfite because of the lignin in the fibers, but in general, the opacity of unfilled papers depends upon the difference in index of refraction between air and cellulose, that is, between 1.00 and 1.53 respectively. In waxed papers, the opacity depends upon the difference in refractive indices between the cellulose, paraffin, and air spaces not occupied by wax, that is between 1.53, 1.43, and 1.00, respectively. Since most of the spaces in a waxed sheet are occupied by wax and there is relatively little difference between the index of refraction of wax and cellulose, unfilled waxed paper is quite transparent. In order to be effective as an opacifying agent, fillers must have an index of refraction which is appreciably greater than that of the surrounding medium. For ordinary papers, clay or other fillers with a relatively low index of refraction are satisfactory. However, for transparent papers, such as glassine, oiled or waxed papers, it is necessary to use fillers with a very high refractive index. Clay is not satisfactory in glassine or similar papers made from highly beaten stock because of the small difference between the refractive index of clay and cellulose. Likewise, clay has relatively little effect on the opacity of oiled or waxed papers because clay has an index of refraction only slightly higher than that of oil or paraffin. The same situation exists in printing papers when partial penetration of oily vehicle into the paper results in a loss in opacity. Hence, only high opacifying pigments such as titanium and zinc are effective in overcoming "show through" in printed papers.

The indices of refraction for a number of the common papermaking pigments are given in Table II, and for some of the other papermaking raw materials in Table III. The difference in refractive index between clay and titanium dioxide explains why titanium dioxide is from 5 to 10 times more efficient than clay in increasing the opacity of paper.

TABLE II
REFRACTIVE INDICES OF THE COMMON PAPERMAKING PIGMENTS

Clay	1.55
Calcium carbonate	1.56
Zinc oxide	2.01
Zinc sulfide	2.37
Lithopone ^a	1.84-2.00
Titanium dioxide, anatase	2.55
Titanium dioxide, rutile	2.70
Titanium barium pigment	1.91
Titanium calcium pigment, anatase	1.87
Titanium calcium pigment, rutile	1.98
Gypsum	1.52
Calcium sulfate, anhydrite	1.58
Calcium sulfite	1.57
Barium sulfate	1.64
Talc	1.57
Asbestine	1.56
Diatomaceous silica	1.45

^a Lithopone is a mixture of zinc sulfide (2.37) and barium sulfate (1.64) usually existing as separate discrete particles, so that assigning a refractive index to the mixture is open to question.

TABLE III
REFRACTION INDICES OF SOME PAPERMAKING RAW MATERIALS

Air	1.00
Water	1.33
Cellulose	1.53
Paraffin	1.47
Starch	1.53
Animal glue	1.53
Linseed oil	1.48

Another method of comparing pigments for their opacifying effect is by their scattering coefficients (*S* values) used in a formula developed by Kubelka and Munk.^{12, 13} The *S* value of a pigment depends upon its particle size, shape, and the difference between its index of refraction and that of the surrounding medium. Steele¹⁴ lists the following scattering coefficients (*S* values) for various pigments (see Ch. XVI) :

¹² M. N. Davis, *Paper Trade J.* 111, No. 14: 184-188 (Oct. 3, 1940)
¹³ D. B. Judd, *Paper Trade J.* 101, No. 5: 58-61 (Aug. 1, 1935)

Pigment	Scattering coefficient
Clay	0.70
Lithopone (29.5% zinc sulfide—70.5% barium sulfate)	0.95
50% Zinc sulfide—50% barium sulfate	1.15
Zinc sulfide	1.45
Titanium dioxide, anatase	2.20

There are, however, no absolute S values for pigments,¹⁵ since this value depends on the method of preparation and use of the pigment.

The opacity increases as the particle size of the pigment is decreased, because smaller particles have more surface planes through which the light must pass and be refracted and reflected. However, pronounced optima in scattering and reflection are obtained as the particle size is decreased. Sawyer¹⁶ points out that for particles finer than the wavelength of light, scattering increases as the particle size increases, whereas for particles coarser than the wavelength of light, reflection decreases as particle size increases. This is illustrated in Figure IX-1, which was taken from Sawyer.

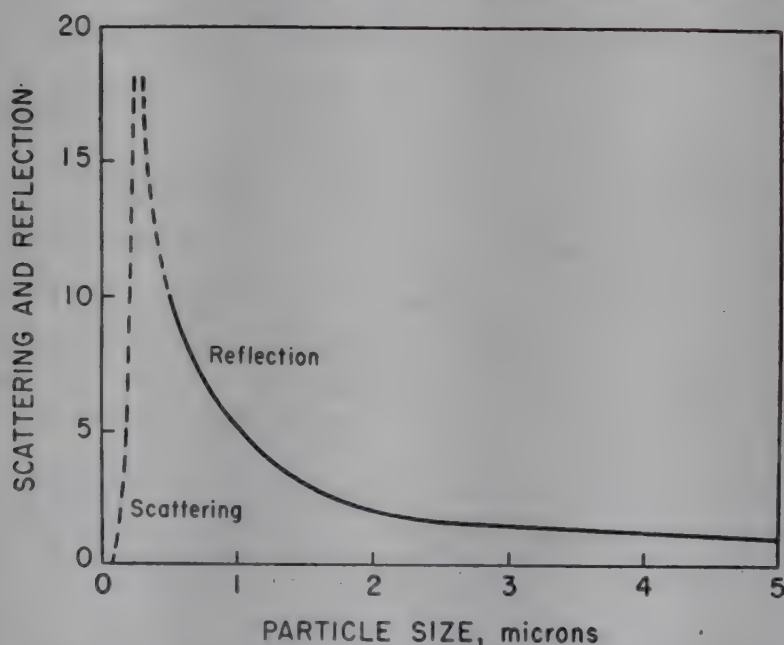


Fig. IX-1. Effect of pigment particle size on the scattering and reflection of light (courtesy R. H. Sawyer E. I. du Pont de Nemours & Co.).

Stutz and Pfund¹⁷ give the correct particle size for maximum coverage and hiding power as approximately one-half the wavelength of the light used in viewing the material. In other words, a minimum of 0.1 to 0.2 micron and a maximum of 0.5 micron are the extremes in particle size for maximum hiding power, as fixed by the wavelength of ordinary light. Stutz

¹⁴ F. A. Steele, *Paper Trade J.* 104, No. 8: 129-139 (Feb. 25, 1937)

¹⁵ A. P. Adrian, *Paper Trade J.* 119, No. 15: 149-155 (Oct. 12, 1944)

¹⁶ R. H. Sawyer, *J. Applied Physics* 13, No. 10: 596-601 (Oct., 1942)

¹⁷ G. F. A. Stutz and A. H. Pfund, *Ind. Eng. Chem.* 19, No. 1: 51-53 (Jan., 1927)

and Pfund found the optimum in scattering for zinc oxide to occur at a particle size of 0.24 micron. For zinc sulfide, the optimum particle size has been found to be 0.25 micron (0.00001 in.).¹⁸ The degree of aggregation of the pigment particles is also important, because any tendency of the individual particles to coalesce into large aggregates will bring about a corresponding reduction in the number of pigment surfaces available for refraction¹⁸ (see Fig. XVIII-27).

Beating decreases the opacity of paper. It is possible, however, to increase the beating and at the same time hold the opacity of the paper by the use of small amounts of certain pigments. In this way, the desirable effects of beating can be obtained without losing opacity. Certain fillers are more effective in increasing opacity in the case of beaten stock than in the case of

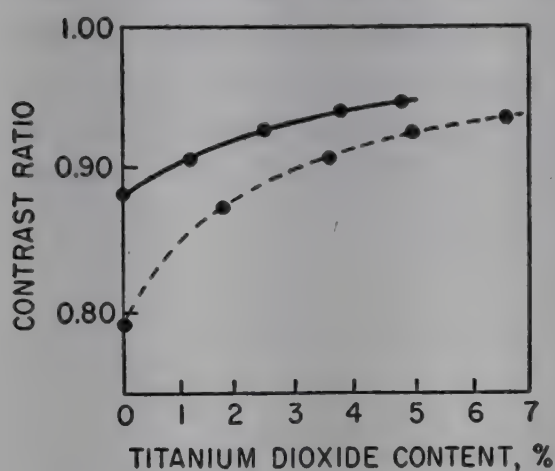


Fig. IX-2. Effect of titanium dioxide on the opacity of (—) unbeaten and (---) beaten (68 Schopper-Riegler) stock.

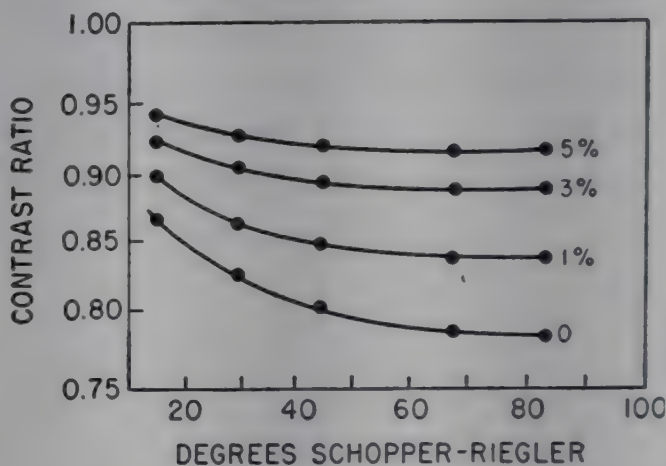


Fig. IX-3. Effect of beating on the opacity of paper containing various amounts of titanium dioxide (given in percentage pigment at right of curves).

unbeaten stock,¹⁹ since it is easier to increase the opacity of a transparent sheet than of one which has a fairly high original opacity. For example, 2% of titanium dioxide would increase the opacity of paper having 50% opacity to about 65% opacity, but would only increase the opacity of paper having 85% opacity to about 90% opacity. However, this increased effectiveness at low original opacity is true only for the pigments of high refractive index (e.g., TiO_2 and ZnS), and not true for pigments of low refractive index (e.g., CaCO_3 or clay). For example, the latter have practically no opacifying effect in glassine. Figure IX-2, taken from published work of Willets,¹⁹ shows the effect of increasing amounts of titanium dioxide on the opacity of paper made from unbeaten and beaten pulp. Figure IX-3, taken from the same article, shows the effect of beating on the opacity. As can be seen from this figure, beating in the presence of a high opacifying pig-

¹⁸ H. M. Cyr, *Paper Trade J.* 96, No. 24: 293-296 (June 15, 1933)

¹⁹ W. R. Willets, *Paper Trade J.* 102, No. 3: 36-39 (Jan. 16, 1936)

ment (e.g., TiO_2) results in only a relatively small reduction in opacity compared with the loss of opacity which occurs on beating an unpigmented furnish. It is possible by combining increased beating with pigmentation to increase both the strength and the opacity of paper. Steele²⁰ points out that the opacifying power of zinc sulfide is approximately ten times that of bleached sulfite pulp, and that a sulfite sheet containing 10% zinc sulfide may owe fully half of its opacity to the pigment. Similarly, about 0.5 to 0.7% pure titanium dioxide is equivalent to approximately 5 lb. basis weight ($25 \times 40\text{--}500$) as far as opacity is concerned.

The subject of opacity is discussed further in Chapter XVI.

Effect on Brightness

White pigments such as calcium carbonate, titanium dioxide, and zinc sulfide strikingly improve the whiteness and brightness of paper, and are

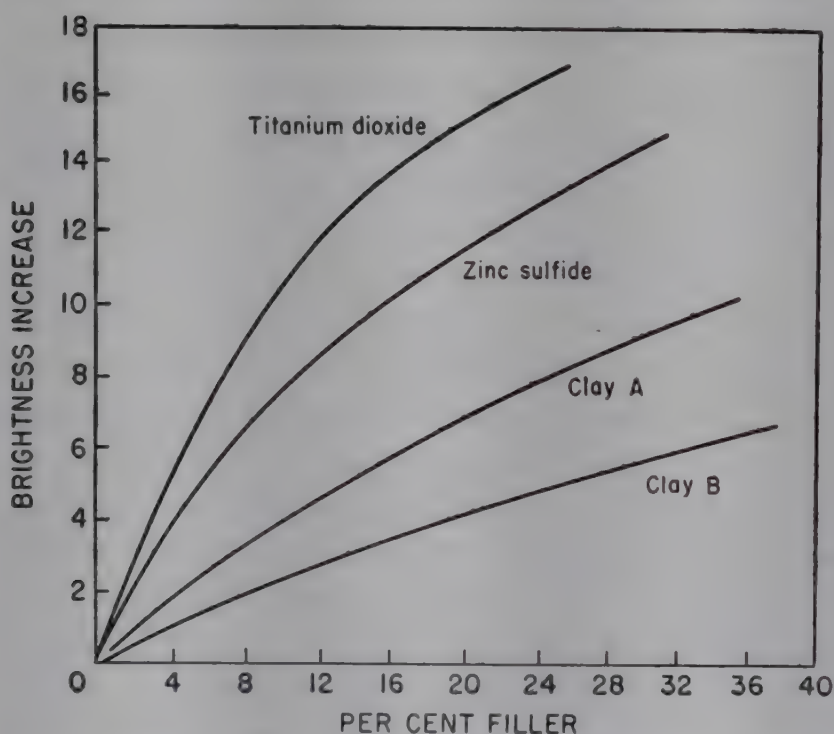


Fig. IX-4. Effect of different pigments on the brightness of paper.

often used to brighten the color of dull paper stock. Soluble dyestuffs have almost completely replaced colored pigments in the production of colored papers, but white pigments remain the only means of brightening paper stock, aside from bleaching.

The increase in sheet brightness obtained by filling depends partly upon the original brightness of the pigment and partly upon the particle size and "covering power" of the pigment. If the pigment is brighter than the pulp, decreasing the particle size will increase the brightness. The curves in Figure IX-4 show the relative brightness obtained with different

²⁰ F. A. Steele, *Paper Trade J.* 104, No. 8: 129-139 (Feb. 25, 1937)

pigments.²¹ Since the actual brightness values of the two clays used in the figure were approximately the same, the difference in their brightening effect on the paper was probably due to a difference in their particle size.

The brightening effect obtained with a given pigment depends upon the original brightness of the unpigmented paper. Stock having a brightness of 50% would be expected to be increased in brightness to a value of about 55% if 2% titanium dioxide were incorporated in the paper. In comparison, stock having a brightness of 90% would be increased in brightness to a value of only about 91.5% when the same amount of pigment was used.

Excessive calendering greatly reduces the brightness of heavily filled papers, particularly clay-filled and, to a greater extent, talc-filled papers. These papers are susceptible to blackening on calendering. White pigments tend to improve the aging qualities of paper, since pigments change less in color on aging than pulp fibers.

Effect on Smoothness and Other Properties

In general, fillers increase the smoothness of the calendered paper, because of the mineral matter filling in the voids on the surface of the paper which results from the responsiveness of filler to action of the calender rolls. On the other hand, Brecht²² found that the smoothness of uncalendered papers was reduced in proportion to the amount of filler in the sheet, with the exception of blanc fixe, which increased the smoothness. Shaw and Simmons²³ found that precipitated calcium carbonate and clay produce about the same smoothness, whereas natural calcium carbonate, titanium dioxide, and zinc sulfide produce papers of lower smoothness values.

The presence of clay in the surface layer of paper increases the oil absorptivity, due to the fact that clay has a greater attraction for oil than the more hydrous cellulose.^{24, 25} This effect is dependent upon the particle size distribution, hydration, and other properties of the clay. Clay also has an appreciable effect on the equilibrium moisture content of paper.²⁶ Because of the effects on smoothness, oil absorption, and moisture content, papers which contain clay generally print better than those made from 100% fiber. Shaw and Simmons²³ rate the various pigments for their effect on increasing the oil penetration in the following decreasing order: precipitated calcium carbonate, natural calcium carbonate, zinc sulfide, titanium dioxide, and finally clay.

²¹ M. N. Davis, *Paper Trade J.* 111, No. 14: 184-188 (Oct. 3, 1940)

²² W. Brecht, *Papier-Fabr.* 33: 398-401 (1935)

²³ M. B. Shaw and R. H. Simmons, *J. Research Nat. Bur. Standards*, Research Paper RP 1180, Vol. 22 (Mar., 1939)

²⁴ J. Strachan, *Paper-Maker* 93, No. 5: 65-67 (May, 1937)

²⁵ B. W. Rowland and H. J. Allison, *Paper Trade J.* 111, No. 3: 25-28 (July 18, 1940)

²⁶ F. C. Clark, *Paper Trade J.* 101, No. 19: 33-35 (Nov. 7, 1935)

Effect on Strength

Fillers tend to reduce the internal strength of paper. The use of 10% clay results in about a 20% loss in bursting strength and a much higher loss in folding endurance. Tearing resistance is not appreciably affected.²⁷ Some pigments apparently do not reduce the strength as much as others, although this is a controversial point among papermakers. Lodge²⁸ reports that talc does not reduce the strength as much as clay. Comparing titanium, zinc, and barium pigments, Crawford²⁷ obtained a progressive loss in strength for an increase in the ash content of the paper, regardless of the pigment used, which is surprising in view of the high molecular weight of barium.

If high percentages of filler are used, the strength may be seriously impaired. In such cases, it may be necessary to use less filler or to change the fiber furnish by incorporating more high-strength fiber into the sheet. Changing from a low-opacifying to a high-opacifying pigment results in less loss in strength, because smaller amounts of pigment will be required to obtain the same opacity and brightness. Reduced filler content means less strength loss, because the filler occupies less volume in the sheet and causes less interference with the internal bonding of the fibrils.

The high specific gravity of titanium and zinc pigments means that these pigments will occupy less volume in the sheet than most pigments for the same weight of added material. According to Cyr,²⁹ paper containing 10% of zinc sulfide by weight will contain only about 1½% of pigment by volume. On the other hand, Hibberd³⁰ reports that titanium dioxide and clay seem to cause about the same reduction in strength when used on an equal weight basis. As a rule, however, titanium-filled papers have a lower ash content and a higher strength than clay-filled papers because of the low percentages of filler used. Pigments of large particle size have a tendency to crush the fibers during calendering when used in large quantities.

Effect on Pitch

Occasionally trouble is experienced with the formation of pitch and rosin spots in the paper during manufacture. Certain fillers, such as diatomaceous silica and bentonite, are sometimes used to combat this condition (see Ch. X). These fillers alleviate the condition by adsorbing the small particles of pitch and keeping the pitch from agglomerating into larger particles which cause trouble. A similar application is the use of fillers in the repulping of asphalt-laminated scrap, where the pigment attaches itself

²⁷ J. J. Crawford, *Pulp Paper Mag. Canada* 37: 97-101, Convention Issue (1936)

²⁸ W. C. Lodge, *Pulp Paper Mag. Canada* 22, No. 4: 102-104 (Jan. 24, 1924)

²⁹ H. M. Cyr, *Paper Trade J.* 96, No. 24: 293-296 (June 15, 1933)

³⁰ A. D. Hibberd, *Paper-Maker* 115, No. 2: 13-20 (Feb., 1948)

to the particles of asphalt, thereby preventing these particles from agglomerating into troublesome size. On the other hand, there is a tendency for pitch troubles to become intensified when alkaline pigments such as calcium carbonate are used in the furnish.³¹

Retention of Pigments

The percentage of pigment added to the pulp system which is held in the dry sheet is referred to as the pigment retention. A high retention is desirable from the standpoint of reducing the loss of pigment, particularly in the case of the expensive pigments such as titanium dioxide and zinc sulfide. However, it is not enough that the pigment be held loosely in the sheet; it must be well anchored to the fiber so that it will not dust out during calendering or printing of the paper.

Pigment retentions as low as 25% used to be obtained, but with the introduction of closed white water systems on the paper machine, retention has improved greatly. Today, it is frequently as high as 85 to 90% of the pigment added to the beater when an efficient water system is used, although an average figure would probably be in the neighborhood of 60 to 70%.

Calculation of Retention

The simplest and most accurate method of calculating retention is to make an ash determination on a sample of stock taken from the beater and on a sample of finished paper taken off the end of the paper machine (see Ch. XVI). After the ash figures have been converted to filler content, the weight of filler appearing in the paper can be divided by the weight of filler in the stock at the beater to give the percentage retention. The retention value obtained in this way indicates the amount of filler lost in the paper-making operation as a whole. If desired, it is also possible to determine the loss in any particular stage of the process by making ash determinations on samples of stock taken just before and just after this stage. The retention value obtained by this method includes the ash content of the fibers and other constituents of the furnish.

In determining the ash content by ignition, notice should be taken of any moisture lost by the pigment and any chemical changes in the pigment taking place at high temperatures, as pointed out in the methods of making ash determinations in Chapter XVI.

Conditions Affecting Retention

Many factors affect retention. In practice, it is known that retention increases with (1) increased sheet weight, (2) increased beating or refining

³¹ H. R. Davidson, *Pulp Paper Mag. Canada* 46, No. 3: 205-211, Sixth Wartime Issue (1945)

of the stock, (3) increased sizing (although this effect is due predominantly to increased alum used), (4) increased fiber length of the stock, (5) increased recirculation of white water, and (6) increased temperature. In general, retention decreases with (1) increased machine speed, (2) increased suction, (3) increased dilution of stock (although this is debatable), (4) increased shake, (5) increased size of wire mesh, and (6) higher pH values. Retention can be measured in the laboratory, but mill tests are much more indicative of the results to be obtained, since the results are affected by so many different machine conditions. However, considerable work has been done on a laboratory scale, and some of the results are reported below.

The retention of pigment usually increases noticeably as the sheet weight is increased. This is shown in Figure IX-5, which illustrates the effect of increased sheet weight on the retention of titanium dioxide. This curve was taken from published work of Willets,³² but Haslam and Steele³³

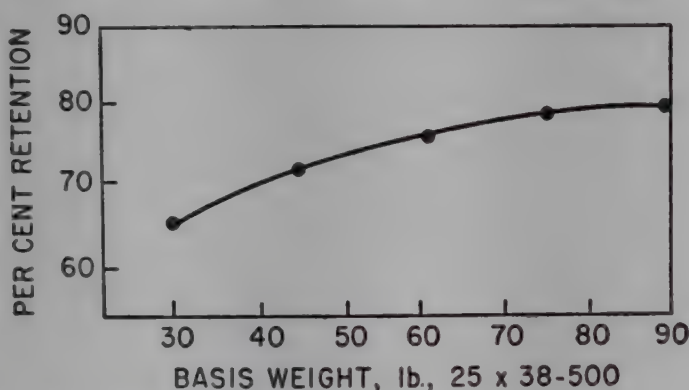


Fig. IX-5. Effect of basis weight on retention of titanium dioxide.

have published a similarly shaped curve (although with much lower corresponding retentions) showing the effect of sheet weight on the retention of zinc sulfide. As can be seen from Figure IX-5, retention falls off rapidly at low sheet weights. Even at very high sheet weights, the retention does not approach 100%.

In general, the retention obtained with different papermaking stocks decreases in the following order: cotton, sulfate, sulfite, and groundwood, which is the order of decreasing fiber length. Well-hydrated stock ordinarily retains pigment better than slightly hydrated stock. This is shown in Figure IX-6, which was taken from data published by Willets,¹⁹ showing the effect of beating on the retention of titanium dioxide. Similar data have also been published for zinc sulfide,³³ and in this case, the curve leveled off quite sharply at a total retention of 18 to 20%. The increased retention which occurs on beating can be explained by the greater surface of the fibers

³² W. R. Willets, *Paper Trade J.* 101, No. 13: 177-182 (Sept. 26, 1935)

³³ J. H. Haslam and F. A. Steele, *Paper Trade J.* 102, No. 2: 22-25 (Jan. 9, 1936)

which is available for adsorption of filler, or it can be explained by the fact that the sheet contains smaller interfiber interstices and thus acts as a more efficient mechanical filter. Another possible factor is that increased beating reduces the velocity of the water removed from the wet sheet on the wire. In unsized papers, the latter two effects are probably much more important than adsorption.

Increasing the amount of pigment added to the stock generally tends to decrease the retention. One exception is calcium sulfate, where the reverse is true. Since one would expect an improved retention for increasing pigment if filtration factors were predominant, it becomes obvious that some other factor more important than simple filtration is involved. On the other hand, retention is low when very small percentages of filler are added because of the high dilution.

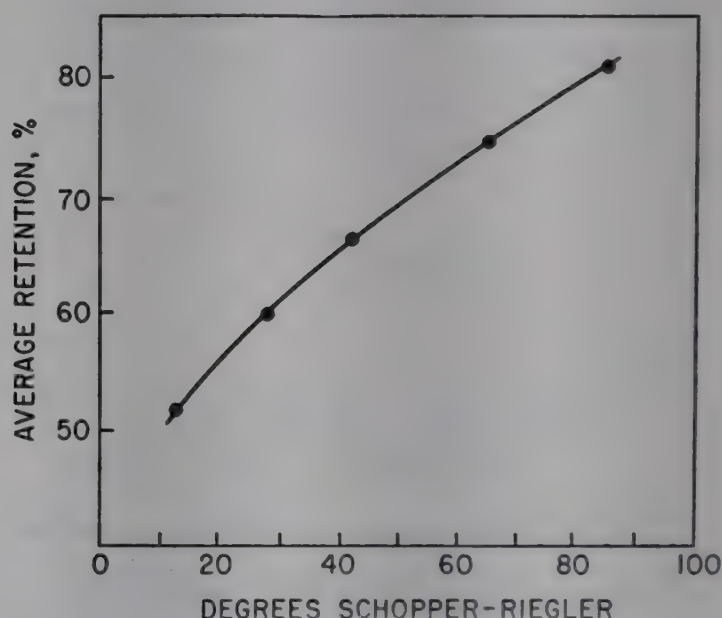


Fig. IX-6. Effect of beating on retention of titanium dioxide.

As a general rule, a reduction in consistency of the stock tends to reduce retention. However, in the case of highly beaten stock, retention is relatively unaffected or slightly increased as the consistency is reduced.

Theories of Retention

There have been a number of different theories to explain retention.³³⁻³⁵ Retention has been explained as being due to: (1) filtration of the pigment particles at the interstices between the fibers, (2) mechanical attachment of the pigment to imperfections in the fiber wall surface, (3) adsorption of the pigment on the fiber surface, (4) capillary attraction of

³⁴ W. Brecht and H. Pfretzschner, *Verein der Zellstoff- und Papier-Chemiker*, pp. 429-439 (1936)

³⁵ S. W. Martin and W. R. Willets, *Paper Trade J.* 110, No. 8: 98-104 (Feb. 22, 1940)

the pigment in the pores of the fiber, (5) diffusion of the pigment into the lumen of the fiber, and (6) coflocculation of the pigment with rosin precipitate or fiber debris. In opposition to the force of retention, there is a force which tends to remove the filler from the sheet. This force is the shearing stress produced by the rush of water through the sheet during formation on the paper machine wire.

There have been two principal theories to explain the retention of pigments, the mechanical and the colloidal theories. These two theories are based upon the relative importance of adsorption forces in comparison with mechanical forces in holding the filler in the paper. It is very probable that retention is a combination of both mechanical and colloidal forces.

Mechanical Theory of Retention. The early paper chemists believed that retention was due mostly to mechanical effects. This was substantiated by work which showed that the highest retention was obtained with pigments of large particle size.³⁶ It is likely that the relatively coarse pigments, such as talc and filler clay, are retained mostly by filtration. Even the finer pigments may be partially retained by filtration, if they have been flocculated by alum so that they have a large effective particle size.

On the other hand, filtration effects are relatively ineffective in a system which consists only of pulp and filler without alum, starch, rosin, etc. This is to be expected, since the filler particles, under such conditions, are much smaller than the pores of the paper. In addition, both the filler and the fibers usually have the same electrostatic charge (negative) and tend to repel each other. As a result, most of the filler passes into the white water. The fact that dilute, well-dispersed suspensions of certain pigments will pass through ordinary filter paper is indicative of the inefficiency of simple filtration.

The increase in retention which normally results from an increase in sheet weight is considered to be a mechanical effect caused by the greater filtering efficiency of the thicker fiber mat. However, a thicker fiber mat means a slower drainage rate, which by itself increases the filler retention, and consequently, increased retention resulting from increased sheet weight may be explained by a change in the rate of drainage.

Most chemists now believe that filtration is of minor importance compared with colloidal effects, so far as total retention is concerned. Albert³⁷ has drawn a sketch, shown in Figure IX-7, using data derived from other sources,³⁸ showing the relative importance of filtration and adsorption ef-

³⁶ R. D. McCarron and B. W. Rowland, *Paper Trade J.* 96, No. 22: 272-275 (June 1, 1933)

³⁷ C. G. Albert, *Paper Trade J.* 105, No. 6: 89-93 (Aug. 5, 1937)

³⁸ W. Brecht and H. Pfretzschner, *Verein der Zellstoff- und Papier-Chemiker*, pp. 429-439 (1936)

fects. It can be seen that filtration is relatively important with coarse fillers, but of little importance with fine fillers. This is further illustrated by the

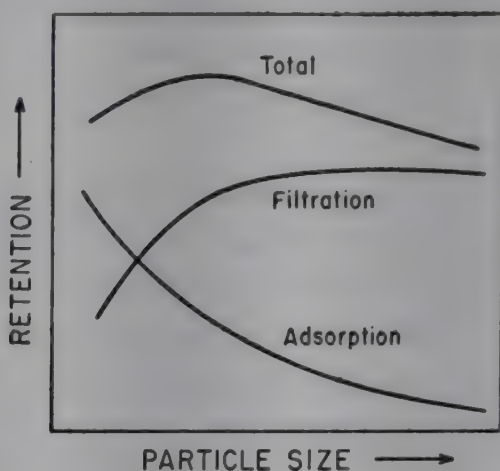


Fig. IX-7. Effect of pigment particle size on the mechanism of retention in paper.

results in Table IV obtained by Roschier³⁹ on clay separated into four particle size fractions by elutriation. As can be seen from this table, the retention of the clay of fine particle size was very low when used in unbeaten, unsized pulp containing no alum. The retention of clay of all sizes was in-

TABLE IV

RETENTION OF CLAY OF VARIOUS PARTICLE SIZES

Pulp	Rosin sizing, %	Alum, %	Per cent retention			
			5 μ	5-12 μ	12-20 μ	20-44 μ
Unbeaten	0	0	8	15	25	32
Unbeaten	0	2	36	34	47	54
Unbeaten	2.3	0.84	28	32	39	42
Unbeaten	2.3	2.5	38	41	49	55
Beaten	2.3	2.5	71	72	74	76

creased by the addition of alum to the furnish, but an especially large increase was obtained in the case of the clay of small particle size. When used in beaten, well-sized stock, there was only a comparatively small difference in retention for clays of different particle size.

Colloidal Theory of Retention. Some pigments, such as zinc sulfide and titanium dioxide, have a very small particle size and yet show a high retention.⁴⁰ With these pigments, retention cannot be due entirely to mechanical filtration, since the pores of the paper are much larger than the pigment particles. The fact that these finer fillers are often retained better than the coarse fillers points to a colloidal rather than a mechanical mechanism of retention.

³⁹ H. Roschier, *Finnish Paper Timber J.*, pp. 192-254 (1927)

⁴⁰ O. Kress and H. M. Cyr, *Paper Trade J.* 96, No. 10: 127-130 (Mar. 9, 1933)

It is now generally recognized that alum plays a major role in retention. As soon as alum is added, colloidal factors become predominant. One colloidal phenomenon involved is a simple flocculation of the pigment particles resulting in an increase in their size. The flocculating effect of aluminum ion on colloidal substances is well known, and the effect on pigments can be readily demonstrated. For example, untreated titanium dioxide suspensions tend to pass through very fine filter paper, but if the suspension is treated with alum, the pigment is retained on the filter paper and the filtrate comes through clear. Alum is particularly effective on clay, where it reduces the concentration of adsorbed ions and the amount of imbibed water, thereby resulting in an increase in the effective size of the clay particles. As a result, the pigment particles are more readily filtered out in the wet sheet on the paper machine. Alum is most effective in improving retention of the finer pigments (see Table IV).

Even more important than the alum itself is the alumina produced by the hydrolysis of the alum. This alumina is adsorbed by the negatively charged fibers, giving them a positive charge which attracts and holds the negatively charged pigment particles. Weber and Shaw⁴¹ found that a deficiency of alumina in the sheet appreciably lowers the retention of titanium dioxide.

Haslam and Steele⁴² observed in the microscope the effect of passing a dilute suspension of zinc sulfide past fibers held on a small hook in a capillary tube and came to the conclusion that pigment particles became strongly attached to the fiber by coflocculation. In other words, the pigment particles became attached to the fiber surface as a result of interfacial forces analogous to those in ordinary flocculation. These forces are relatively weak, and consequently the pigment is fairly easily removed from the sheet during sheet formation. This causes two-sidedness, due to preferential removal of pigment from the wire side of the sheet. In addition, the fibrils and fiber debris are often more heavily pigmented than the fiber itself, and these tend to be sucked from the sheet, thereby contributing to two-sidedness. In addition to coflocculated pigment, Haslam and Steele also observed the presence of "mechanically attached" pigment existing within the fiber lumen. This pigment is retained in the sheet upon repeated washings and, in the case of papers filled with zinc sulfide under laboratory conditions, tends to reach a constant value of about 50% of the original pigment added to the furnish. The amount of mechanically attached pigment can be increased by beating.

It is likely that pulp fibers have a capacity for retaining only so much pigment by colloidal forces. This would account for the fact that retention

⁴¹ C. G. Weber and M. B. Shaw, *Paper Ind.* 28, No. 8: 1137-1140 (Nov., 1946)

⁴² J. H. Haslam and F. A. Steele, *Paper Trade J.* 102, No. 2: 22-25 (Jan. 9, 1936)

falls off as higher percentages of pigment are added. Fair⁴³ has pointed out that in a closed system, the first paper run over the machine may show a retention of only 20 to 25% and that this may build up on prolonged operation to a retention of 50 to 60%. The low original retention may indicate the amount of pigment held by colloidal forces. The difference between this amount and the final retention may indicate the retention due primarily to filtration effects.

Effect of Order of Addition and Amount of Alum

Fillers should be furnished to the beater before the alum is added in order to insure even distribution of the pigment in the stock before flocculation is brought about by the alum. For best results, the alum should be added at the point of maximum dilution and sufficient time allowed for floc formation before the sheet is formed.⁴⁴ Some mills obtain the best results

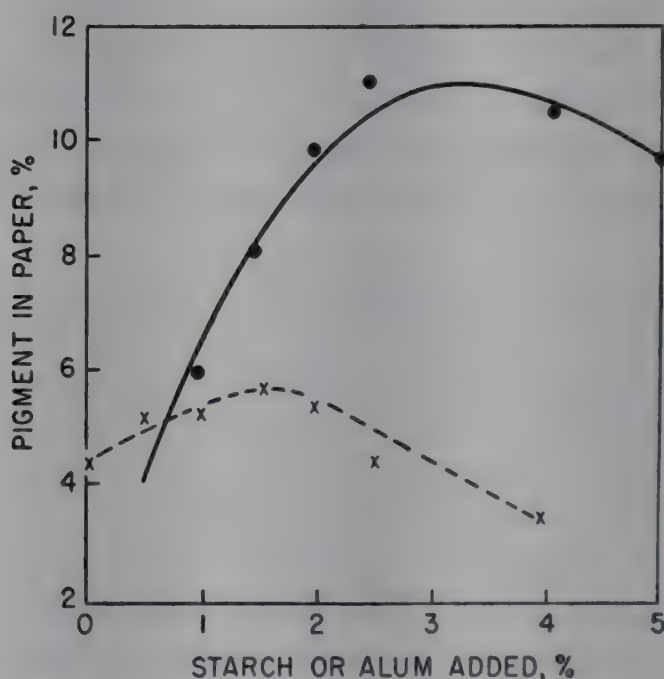


Fig. IX-8. Effect of alum (—) and starch (--) on retention of zinc sulfide pigment.

by adding the alum just before the stock goes to the headbox of the paper machine. Poor retention results if the pigment is added after the alum, although the opacity obtained per unit of pigment actually present in the paper is apparently highest under these circumstances.⁴⁵

There appears to be an optimum amount of alum for maximum retention. Willets⁴⁶ found 3% alum to be most effective with titanium pigments. Haslam and Steele⁴⁷ also found 3% alum to be most effective with zinc sul-

⁴³ A. E. H. Fair, *Paper Trade J.* 103, No. 21: 311-312 (Nov. 19, 1936)

⁴⁴ L. B. Miller, *Paper Trade J.* 108, No. 2: 18-24 (Jan. 12, 1939)

⁴⁵ J. J. Crawford, *Pulp Paper Mag. Canada* 37: 97-101, Convention Issue (1936)

⁴⁶ W. R. Willets, *Paper Trade J.* 102, No. 3: 36-39 (Jan. 16, 1936)

⁴⁷ J. H. Haslam and F. A. Steele, *Paper Trade J.* 102, No. 2: 22-25 (Jan. 9, 1936)

fide as shown in Figure IX-8. Brecht⁴⁸ found 3% to be optimum, but Roschier^{49,50} found 5% alum to be most effective when the pH was maintained constant at 5.6. Roschier found that pH had an important effect, even with constant alum. Alum without alkali is probably not very effective, since no alumina is formed. The optimum pH appears to be between 5 to 6.

Effect of Pigment Properties on Retention

Two physical properties of the pigment which generally make for increased retention are low specific gravity and low solubility in water. Blanc fixe (barium sulfate) has a high specific gravity (about 4.5) and consequently is poorly retained and produces more pronounced two-sidedness than the lighter pigments, such as clay. High density is not always the most important factor, but it is important in the case of barium sulfate. Soluble fillers, such as calcium sulfate, show low retention. In general, clays are fairly well retained, but usually show lower retention than titanium dioxide and asbestine.

Particle shape is a factor with talc, since the fibrous talcs are better retained in the sheet than the non-fibrous talcs and other fillers. Particle size is important, and it has been pointed out that large particle size does not always favor high retention, since titanium dioxide often shows a higher retention than clay, even though it has a smaller particle size.⁵¹ Cyr⁵² reports that retention is higher with zinc sulfide of small particle size than it is with the same pigment of larger particle size. In the case of clay, the smaller particles are often better retained than the coarser particles, but the highest retention is generally obtained at an intermediate particle size (see Fig. IX-7). Pigments of large particle size are retained almost entirely by filtration, whereas those of small size are retained to a large extent by adsorption. Davidson⁵³ reports that calcium carbonate gives best results with an average size of 10 to 40 microns, since finer particles cause dusting difficulties and coarser particles are removed in the screening operations. From a practical papermaking standpoint, it is possible to obtain high retention with pigments in a wide range of particle size, although, as shown above, the mechanism of retention is different.

⁴⁸ W. Brecht, *Papier-Fabr.* 33: 398-401 (1935)

⁴⁹ H. Roschier, *Finnish Paper Timber J.*, pp. 192-254 (1927)

⁵⁰ H. Roschier, *Papier-Fabr.* 24, No. 23: 348-350; No. 24: 363-365; No. 25: 384-388 (June 6, 13, 20, 1926)

⁵¹ W. R. Willets, *Paper Trade J.* 101, No. 13: 177-182 (Sept. 26, 1935)

⁵² H. M. Cyr, *Paper Trade J.* 96, No. 24: 293-296 (June 15, 1933)

⁵³ H. R. Davidson, *Pulp Paper Mag. Canada* 46, No. 3: 205-211, Sixth Wartime Issue (1945)

Effect of Other Substances on Retention

Rosin size itself has comparatively little effect on retention.^{54, 55} However, when used with alum, rosin size tends to increase retention, although exceptions with talc and titanium dioxide have been reported. In those cases where rosin size increases the retention, it is probably due to the formation of rosin size precipitate, inasmuch as the addition of rosin size does not improve retention unless alum is also added.

Starch has been reported as being both beneficial and harmful to retention, but in general, starch exerts a negligible effect in comparison with that of alum.⁵⁶ In some cases, a small amount of starch increases retention, whereas large amounts decrease retention as shown in Figure IX-8.

Colloidal glue is effective in increasing retention because of its flocculating effect on pigment particles. A specially prepared colloidal glue (Sveen glue) is widely used for increasing the retention of fillers (see Ch. VIII). Other substances which have been used to increase retention are sodium silicate and sodium aluminate, but these substances are effective only if used with alum.

Distribution of Loading in the Sheet

Much of the pigment in the sheet adheres to the surface of the fibers, although even in heavily filled sheets, the fibers are by no means covered. Some of the finer fillers may find their way into the interior or lumen of the fiber. Haslam and Steele⁵⁷ estimate that commercial papers filled with zinc sulfide may contain upward of 30% of the pigment in the lumen of the fibers, but this is probably not the case with the coarser pigments.

Most heavily filled papers show two-sidedness, the wire side of the sheet generally containing less pigment than the felt side. Schultz⁵⁸ examined a number of filled papers by separating them into three layers, and although he found that the majority contained a higher percentage of pigment on the top side, a few contained more pigment on the wire side, and some showed a uniform distribution throughout. In the case of one filled paper, the felt side was found to contain 27% ash, while the wire side contained only 6.5% ash, the samples having been obtained for analysis by scraping the two sides of the sheet with a razor blade.^{58a} Laboratory hand-sheets have a somewhat different distribution of filler, as shown by Han-

⁵⁴ S. W. Martin and W. R. Willets, *Paper Trade J.* 110, No. 8: 98-104 (Feb. 22, 1940)

⁵⁵ W. R. Willets, *Paper Trade J.* 101, No. 13: 177-182 (Sept. 26, 1935)

⁵⁶ W. Brecht, *Papier-Fabr.* 33: 398-401 (1935)

⁵⁷ J. H. Haslam and F. A. Steele, *Paper Trade J.* 102, No. 2: 22-25 (Jan. 9, 1936)

⁵⁸ F. Schultz, *Papier-Fabr.* 35, No. 51: 516-518 (Dec. 22, 1937)

^{58a} *Allg. Papier Rundschau* No. 15: 731 (Nov. 30, 1949) through *B.I.P.C.* 20: 650-651 (1950)

sen,^{58b} who found that the filler content was lowest on the felt side and highest in the middle of the sheet.

Mon⁵⁹ found that the distribution of pigment in the sheet depends upon the type of stock and the method of fiber preparation. He found that the papers which contain less pigment on the felt side are generally made from stock which is groundwood free, contains a high percentage of rosin size, and is well beaten. On the other hand, the papers which contain a lower percentage of filler on the wire side are generally made from stock which has a high groundwood content, contains only a small amount of rosin size, and is formed on the machine at high speed. High machine speeds and increased suction are two very important conditions which promote two-sidedness.

In many cases, it is desirable to add pigment preferentially to one side of the sheet. Coating with pigment is one method of doing this, and this operation is discussed in Chapter XVIII. In lined boards made on the cylinder machine, fillers are frequently added to the liner stock to increase the opacity and the brightness of the liner, and hence the over-all brightness of the board. It is easier to increase the brightness of paperboard by adding pigment to the liner than by incorporating it throughout the various filler plys.⁶⁰

^{58b} E. Hansen, *Tappi* 34, No. 4: 180-185 (Apr., 1951)

⁵⁹ F. V. Mon, *Papeteries Belge* 18: 101-105 (Feb., 1938)

⁶⁰ W. R. Willets, R. T. Bingham and L. H. Ericksen, *Paper Trade J.* 109, No. 23: 308-310 (Dec. 7, 1939)

INTERNAL SIZING

The permeability of paper to fluids (whether gases or liquids) is a very important property. It is of great practical importance for blotting papers, writing papers, toweling, wrapping and packaging papers, insulating papers, printing papers, and many other grades. Each of these different grades must meet standards of permeability, depending upon the use to which the paper is put.

Introduction to Sizing

This chapter and the following chapter on surface sizing are primarily concerned with the resistance of paper to the penetration of liquids, whether the liquids are aqueous writing inks, non-aqueous printing inks, blood, or just plain water. Papers which are resistant to liquids are called sized papers, whereas those which are lacking in resistance are called unsized papers. As a rule, the papermaker refers to paper as being hard (strongly) sized, slack (weakly) sized, or water leaf (unsized).

Definition of Sizing

The term "sizing" is a loose term. It is used, as mentioned above, to express resistance to the penetration of liquids, such as water or writing inks. In this sense, the term refers to a property of the paper, but it is also used as descriptive of the process for obtaining resistance to liquid penetration.

Because of the broad meaning of the word "sizing" as now used, it is better practice, when referring to the properties of paper, to use more precise terms which distinguish between the different sizing properties. Some of these more precise terms are water repellency, water resistance, oil resistance, and ink resistance. Water repellency is characterized by resistance to wetting by water, i.e., a "duck's back" effect. Water resistance or water-proofness refers to the ability to retard the penetration of liquid water, even though the surface of the paper "wets" fairly well. Moisture-vapor resistance is sometimes confused with these two terms, but it is an entirely different property which refers to the resistance of the paper to the passage of water in the vapor state. The property of water vapor resistance is discussed in Chapter XVIII since it is ordinarily not considered as a sizing effect.

Sizing Processes

The two principal sizing processes are internal sizing and surface sizing. Internal sizing consists of mixing the sizing agent with the fibrous furnish and forming the entire mass into a sheet containing a relatively uniform distribution of fibers and sizing agent. Surface sizing, on the other hand, involves the application of sizing agent to the surface of the already formed paper. Surface sizing is usually done in a size tub, size press, or on the calenders. Surface-sized papers generally contain internal size. The process of surface sizing is discussed in the next chapter.

Relationship between Sizing and Other Papermaking Subjects

The subject of sizing is closely related to many other subjects in papermaking. Sizing is a factor in the printing of papers. It is an important property of protective wrapping papers for greasy, oily, or moist foods. Sizing is also of great importance in such operations as coating and laminating, inasmuch as the degree of sizing determines the extent of penetration of adhesive in these operations.

Treatment of paper with internal sizing agents not only affects the sizing of the paper, but also has a definite effect on other properties of the paper. Excess internal size (rosin) in the paper tends to lower the brightness of the paper and also to lower the burst, tensile, tearing and folding strengths of the paper, although folding strength may be increased slightly with small additions of rosin size. Internal size (rosin) also lowers the permanence of the paper, since it produces discoloration and loss of strength on aging. Deterioration is particularly rapid in the presence of ferrous iron. These harmful effects are not due entirely to the sizing agent, but rather can be attributed in a large measure to the acidity of the paper arising from the alum added with the size.

Types of Sizing Agents Used

The various sizing agents used in the paper industry cover a wide range of materials, including animal glue, rosin size, synthetic resins, casein, polyvinyl alcohol, starch, wax emulsions, and many more similar substances. Some of these, such as rosin size, are used exclusively as internal sizing agents, while others, such as animal glue, are used almost entirely as surface-sizing agents.

In some cases, colloidal materials are used in papermaking for reasons other than their sizing effect, for example, to increase the fiber bonding, to improve the dispersion of the fibers, or to increase the retention of fillers. Starch, glue, vegetable gums, and sodium silicate are some of the materials which are used for these purposes. These materials are sometimes referred

to as sizing agents, but they are discussed in other chapters (such as the chapters on fiber bonding and sheet formation), since their effect on the sizing of the paper is negligible. However, when starch, glue, etc., are used for surface sizing, they may properly be considered as sizing agents.

Rosin size and wax emulsions are the two principal materials used for the internal sizing of paper. Other materials may be used in small quantities as a size additive. Among these is a special polycarboxylic acid, a rosin-maleic anhydride condensation product, sold under the trade name of Mersize. Sodium stearate is sometimes used in the sizing of photographic papers where a chemically inactive sizing agent is required. However, rosin size remains by far the most important internal sizing agent.

Commercial Grades of Sized Papers

Nearly all grades of paper are sized to some extent and must meet definite sizing requirements. The final results depend, to a large extent, upon the type of sizing agent used and the method of applying the sizing agent.

Protective wrapping papers and bag papers must be well sized to preserve the strength of the paper in the presence of water by preventing or inhibiting the absorption of water by the paper. In raw stock for pigment coating, the sizing value of the paper must be maintained at the proper level to control the depth of penetration of water and adhesive into the base paper during coating, thus controlling the strength and other properties of the coating. In security papers, the degree of sizing must be maintained at the

Paper grade	Principal type of sizing	Purpose of sizing
Drawing papers	Internal and surface sized	To prevent too rapid absorption of aqueous ink or paints; to improve finish and strength; to improve erasability; to prevent feathering when ink is used
Writing papers	Internal sized and surface sized	To prevent feathering and penetration of ink; to improve strength, finish, and rattle
Forms	Internal sized	To reduce ink absorption
Chart papers	Internal sized and surface sized	To prevent feathering and penetration; to reduce expansion of paper
Offset lithographic papers	Internal and surface sized	To prevent too much absorption of dampening water and loosening of surface fibers during printing
Kraft wrapping papers	Internal sized	To provide water resistance and protect contents of paper; to prevent loss of strength of paper
Hanging (wall) papers	Internal sized	To improve printing; to retain strength of sheet during pasting and hanging
Coating rawstock	Internal sized	To control the penetration of the adhesive in the coating into the paper
Liners used in laminated boards	Internal sized	To control the penetration of the laminating adhesive
Varnish papers	Surface sized (often coated)	To prevent excessive penetration of varnish

proper value in order that the ink may penetrate into the paper to a depth sufficient to bring about reaction with the security chemicals, but not so far that the writing qualities of the paper are impaired. Some of the different grades of commercial papers which are sized are listed here, along with the reasons for sizing each grade.¹

Bond and writing papers are examples of papers which are ordinarily well sized with rosin size and usually are surface sized with animal glue or starch. The 100% rag content bonds are partly sized with rosin size and then surface sized with animal glue, whereas the rag content and bleached chemical wood pulp papers are partly sized with rosin size and then surface sized with starch or with starch-glue mixtures. Most papers of this grade must not exceed maximum extractable rosin contents. For example, certain users of paper have the following specifications:

100% rag	Maximum rosin content of 1.0-1.2%
Rag content	Maximum rosin content of 1.5-2.0%
100% sulfite	Maximum rosin content of 2.0%

Properties That Affect Sizing

Many fundamental properties go to make up the final sizing value of paper. It is interesting and helpful to study these properties individually, although from a practical standpoint, empirical tests are universally used as a convenient means of measuring the sizing value.

All empirical sizing tests are dependent upon a number of variables. Many of these variables pertain to the properties of the test fluid, such as its viscosity, temperature, and colloidal properties. Other variables pertain to the physical properties of the paper. So many different paper properties influence the sizing value that two sheets with the same sizing value may have entirely different physical properties.

Surface Tension Effects

The wetting and spreading characteristics of the liquid with which the paper is brought into contact plays an important part in determining the sizing value. In order that any liquid may spread along the fiber surface, the surface tension of the liquid must be less than its adhesive tension for the fiber or, in other words, the affinity of the liquid molecules for each other must be less than the attraction of the liquid molecules for the fiber. Stated differently, the surface tension of the fiber surface must be greater than the sum of the surface tension of the liquid, plus the interfacial tension, in order for the liquid to spread and produce a uniform film. If the surface

¹ "Report of Paper Testing Committee on Sizing," *Paper-Maker* 114, No. 3: 22-28 (Sept., 1947)

tension of the fiber surface is less than the combined liquid and interfacial tensions, a definite angle of contact will be formed between the liquid and the fiber, and the size of this angle will depend upon the difference in tensions.

Sizing agents increase the angle of contact formed between water and paper. Thus, a measure of the contact angle furnishes a fairly simple and reliable means of measuring the sizing value. The method of measuring contact angle is described later as one of the important methods of measuring the sizing of paper.

The rate of penetration of liquids into paper depends upon the ratio between the surface tension of the liquid and the contact angle formed between the liquid and the fibers. Surface tension, or capillary suction, as it is sometimes expressed, is the force that tends to pull the liquid into the capillaries of the sheet. The contact angle determines the component of the capillary suction that is effective along the axis of the capillary or, in other words, the component of the force tending to draw the liquid into the sheet. Because sizing agents increase the contact angle, they reduce the component of the capillary force drawing inward. At a contact angle of 180° , the capillary suction becomes zero and the fluid does not penetrate at all.

The addition of wetting agents to the penetrating fluid reduces the angle of contact, which increases penetration, but at the same time reduces the surface tension (capillary suction), which decreases penetration. Thus, the addition of wetting agents both favors and hinders penetration. By way of example, Wilson and Duston² found on unsized papers (zero angle of contact) that the addition of wetting agents to water reduces the penetration because of surface tension lowering. On the other hand, wetting agents result in a greatly increased rate of penetration on sized papers because of their effect in reducing the contact angle.

For most applications, the paper chemist is interested in the rate of penetration of fluids into paper, rather than in the rate of flow through the paper. There is considerable difference between these two properties. The initial penetration is greatly affected by the rate of wetting of the fibers by the penetrating liquid. However, once the fiber surface is wet, water flows through the paper much more readily than in the initial penetration, and the amount of flow depends upon the rate of removal of liquid from the other side of the sheet.

Effect of Porosity

Paper may be considered as a capillary system of interconnecting pores which are irregular in size and shape. The system consists of relatively

² W. S. Wilson and H. E. Duston, *Paper Trade J.* 117, No. 21: 223-228 (Nov. 18, 1943)

large interfiber pores and much smaller intra-fiber pores and crevices which exist within the fiber itself. In order for a liquid to penetrate paper, it must pass through this system of capillary pores, and consequently the porosity or the size of the pores in the paper is an important factor affecting the sizing value. Most of the penetration undoubtedly takes place through the interfiber pores because of their larger size, compared to the intra-fiber pores. However, the latter are of some importance, since most of the fibers lie in the plane of the sheet and hence present their intra-fiber pores to the liquid when it first contacts the sheet.

Effective sizing depends upon having a small capillary pore size, inasmuch as capillary suction is inversely proportional to the effective pore diameter (the rate of flow being inversely proportional to the diameter).³ According to Wilson and Duston,⁴ a variation in pore diameter between 1 to 30 microns means that the capillary suction would vary from 3,000 to 100 cm. of water pressure at zero contact angle.

Thickness of Paper

The thickness of paper is an important factor in determining the length of time required for a given liquid to penetrate completely through the paper. Theoretically the time for penetration should increase as the square of the sheet thickness, but in the case of aqueous penetrants, this is true only for slack and moderately sized papers, and not for hard-sized papers.⁵ With hard-sized papers, sizing increases more nearly as the cube of the sheet thickness, probably due to the fact that a higher percentage of penetration takes place through the intra-fiber pores. On the other hand, the resistance of paper to penetration of oily vehicles varies as the square of the sheet thickness.⁶

The results of most sizing tests are greatly magnified with increasing thickness of the paper. Wilson⁷ states that the only sizing test not affected by sheet thickness is the equilibrium water pick-up. In studying the effect of sheet thickness on sizing value, it should be remembered that there is a difference between Fourdrinier papers and papers made on a multicylinder machine, since the latter are made of several plies which sometimes contain different amounts of rosin size. In some grades of board, all the plies are well sized in order to prevent one ply from acting as a wick and sucking

³ W. S. Wilson and H. E. Duston, *Paper Trade J.* 117, No. 21: 223-228 (Nov. 18, 1943)

⁴ W. S. Wilson and H. E. Duston, *Paper Trade J.* 117, No. 21: 223-228 (Nov. 18, 1943)

⁵ W. S. Wilson and H. E. Duston, *Paper Trade J.* 117, No. 21: 223-228 (Nov. 18, 1943)

⁶ G. L. Larocque, *Pulp Paper Mag. Canada* 39, No. 2: 106-119 (Feb., 1938)

⁷ W. S. Wilson, *Paper Ind.* 30, No. 10: 1514-1522 (Jan., 1949)

water into the sheet, thereby resulting in a general weakening of the paper. On other grades, such as patent coated board, the inner plys are only lightly sized, or not sized at all, whereas the outer ply is hard sized, because normally the outer ply is the only one likely to be exposed to water.

Rate of Penetration (Formula)

So far, penetration has been discussed mostly from a qualitative standpoint. It is possible, however, to express the rate of penetration of liquids into paper in quantitative fashion, using the formula⁸ given:

$$l^2 = \frac{r\sigma \cos \theta t}{2\mu}$$

where l is the depth of liquid penetration in centimeters, r is the pore radius in centimeters, σ is the surface tension of penetrating liquid in dynes per centimeter, θ is the contact angle, t is the time of penetration in seconds, and μ is the coefficient of viscosity of liquid in poises. This formula is satisfactory only for true liquids and does not hold for the penetration of colloidal fluids.

The rate of penetration is greatly influenced by the temperature of the penetrating liquid, due principally to the reduction in viscosity of the liquid at high temperatures. Wink and Van den Akker⁹ found, in their studies on the penetration of water into insulating board, that an exposure of one hour at 130° F. is equivalent to an exposure of three hours at 120° F., or to an exposure of sixteen hours at 100° F.

Sizing against Water

Cellulose fibers always contain some water, and consequently paper is never entirely free of water. The water-absorbing property of cellulose is an advantage in blotting tissue and toweling. In fact, a certain amount of water (moisture) is desirable in all papers, since overly dry fibers are brittle, and sheets formed from them are lacking in strength and pliability. On the other hand, too much water in the paper is undesirable, since it results in a flabby sheet of low strength.

Water may exist in paper in three states, namely colloidal, capillary, and imbibed water (see Ch. I), depending upon the amount present. There is no difference in the final state of the water in the paper, regardless of whether the water is absorbed in the form of liquid water or in the form of vapor, since water absorbed as vapor condenses in the capillary structures of the sheet and functions in the same way as liquid water. For any condition of relative humidity, paper will assume a corresponding specific

⁸ R. M. Cobb and D. V. Lowe, *Tech. Assoc. Papers* 17: 290-293 (June, 1935)

⁹ W. A. Wink and J. A. Van den Akker, *Paper Trade J.* 127, No. 10: 371-376 (Sept. 2, 1948)

moisture content within the hysteresis limits, if the paper is exposed long enough to reach a state of equilibrium.

Paper made from untreated cellulose fibers has very little resistance to the passage of liquid water, since the fibers are hydrophilic (water loving) and form a porous structure which is receptive to water. In this condition, paper has only a limited usefulness, inasmuch as it will pick up any free water with which it comes into contact thereby losing its strength, stiffness, etc. Hence, most commercial papers are sized with rosin size to reduce the permeability to water.

Sizing with rosin size does not decrease the porosity of paper significantly, but rather brings about changes in the wetting properties of the fibers, resulting in a large increase in the angle of contact between the fibers and water. In rosin sizing, the rosin size precipitate is "fixed" on the fibers where it makes the fibers hydrophobic (water hating). In wax sizing, the wax particles are coagulated and "fixed" on the fibers where they, too, increase the water repellency of the fibers. Complete fiber coverage is not attained, but the particles of precipitate are close enough in a well-sized paper to retard the wetting of the fibers by water. The higher the percentage of sizing agent in the paper, the greater the area of fiber which is covered and the longer it takes for the water to pass between the precipitated particles of sizing agent on the fibers and wet the fiber surface. In slack-sized papers, the size is less effective, because the individual particles of the sizing agent are too far apart to protect the fiber from the water adequately and, as a result, the water passes fairly readily between the rosin particles. Once the fiber surface is wet, water forms a zero angle of contact, regardless of how well sized the fibers were originally.¹⁰ The size precipitate has relatively little effect on the amount of water vapor absorbed or the rate of water absorption, even in highly sized papers.

An important factor in sizing against water is the effect which water has on the swelling of the fibers in the paper. In studying the penetration of aqueous liquids into surface-sized papers, Vincent¹¹ found that the rate of penetration is rapid at first, but soon falls almost to zero, on account of swelling of the fibers and the surface-sizing material, thereby reducing the effective pore radius.

Sizing against Organic Liquids

Rosin sizing increases the angle of contact between the fiber surface and water, because water is polar and the rosin size precipitate on the fibers is relatively non-polar, and thus the two tend to repel each other. The effect is entirely different when rosin-sized papers are brought into contact

¹⁰ J. E. Foote, *Paper Trade J.* 109, No. 14: 182 (Oct. 5, 1939)

¹¹ H. L. Vincent, *Paper Trade J.* 110, No. 22: 293-297 (May 30, 1940)

with relatively non-polar liquids such as toluene, alcohols, benzene, and oils, since these liquids form a zero angle of contact with rosin-sized papers. It has been reported¹² that rosin size actually facilitates the penetration of oil-base printing inks. Consequently, some method of sizing, aside from sizing with rosin, must be used when it is desirable to reduce the penetration of printing inks or other oil-base materials. Normally, surface sizing is employed in such cases, and therefore the subject is discussed in the following chapter on surface sizing. The penetration of printing inks is discussed in the chapter on printing (Ch. XIX).

Alcoholic and other non-aqueous liquids generally penetrate paper at a greater rate than aqueous solutions, even in the case of unsized papers. An important factor in the penetration of non-aqueous liquids is the moisture content of the paper, because moisture causes expansion or contraction of the fibers, thereby affecting the porosity of the paper. Thus, when penetration is to be measured with non-aqueous liquids, the moisture content of the paper should be controlled at a constant value by conditioning the paper in an atmosphere of controlled relative humidity before testing.

Sizing against Colloidal Solutions

Sizing against colloidal solutions (writing ink or blood) is quite different from sizing against water, since the penetration of colloidal solutions into paper is affected by factors which have no influence on the penetration of water. Sizing against colloidal solutions may be as much a matter of coagulating the dispersed particles in the solution as of reducing the penetration of the liquid or water phase. Consequently, there is no correlation between the penetration of water and the penetration of colloidal solutions, and for this reason, paper should be tested against the type of liquid with which it is likely to come into contact during use. Thus, writing papers are frequently tested against writing inks, and butchers' wrap is commonly tested against blood or blood serum.¹³ There is, as would be expected, a correlation between the resistance to ink and the resistance to blood, and many mills making butchers' wrap use the ink resistance test as a control measure and test selected samples with blood.

In the case of writing papers, sizing is necessary to keep the ink on the surface and prevent it from being excessively absorbed or spread over the surface of the paper. It is not necessary that the paper be impervious to the whole ink, since the desired results can be obtained by coagulation of the dye particles. Thus, even though the water molecules penetrate rapidly into the paper, no "feathering" of the ink will result if the dye in the ink is

¹² J. E. Foote, *Paper Trade J.* 109, No. 14: 182 (Oct. 5, 1939)

¹³ C. E. Libby and L. Parkinson, *Paper Trade J.* 96, No. 18: 229-232 (May 4, 1933)

coagulated at or near the surface of the paper. This ability of the paper to coagulate colloidal particles is an important factor in those grades of paper used in contact with blood, surface-sizing agents, certain developer solutions, or other similar colloidal solutions. According to Wilson,¹⁴ a hard-sized paper is able to bind or coagulate colloidal particles equivalent to ten times its liquid-holding capacity.

The coagulation of colloidal particles may be brought about by the electrostatic charges on the fibers, or as others believe, by the action of aluminum ions present on the rosin-sized fibers. Because the penetration of water is not affected by these actions, it is possible to increase the ink resistance of paper long after there is any effect on the water resistance by increased additions of rosin size and alum to the paper. The difference between the penetration of water and the penetration of writing ink into papers containing increasing amounts of rosin size is shown in Figure X-1

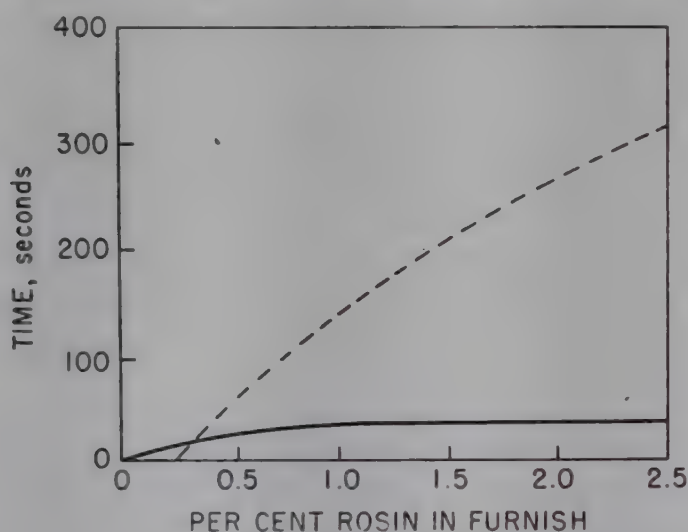


Fig. X-1. Effect of increased rosin size on water (—) and ink (--) penetration.

when tested by the flotation method.^{15, 16} The results show that the resistance to water penetration reaches a maximum very quickly at around 1% rosin, whereas the resistance to ink penetration increases continuously with increasing rosin size. Similar results are shown in Figure X-9.

When paper is brought into contact with writing ink, the dye particles in the ink are coagulated near the surface of the sheet, whereas the clear liquid in the ink tends to pass on through the paper.¹⁷ If a sheet of paper floated on ink is removed and torn just as the clear liquid reaches the top surface of the paper, it will be found that the top part of the sheet contains no ink. Thus, if dry indicator powder is used for indicating the end point, the powder will be changed in color by the water passing through the paper

¹⁴ W. S. Wilson, *Paper Ind.* 30, No. 10: 1514-1522 (Jan., 1949)

¹⁵ W. S. Wilson, *Paper Trade J.* 128, No. 5: 40-44 (Feb. 3, 1949)

¹⁶ W. S. Wilson, *Paper Trade J.* 126, No. 21: 245-250 (May 20, 1948)

¹⁷ W. S. Wilson, *Paper Trade J.* 123, No. 24: 198-202 (Dec. 12, 1946)

before the dye particles in the ink have reached the surface. On the other hand, if the end point is taken as the appearance of dye particles on the top surface of the paper, an entirely different end point is obtained. This illustrates the importance of selecting the proper test procedure for measuring sizing value which should be determined according to the end use of the paper.

Swelling of the paper is an important factor in the penetration of colloidal solutions. When paper is brought into contact with ink, the water and ink penetrate the paper very readily at first, but the rate of penetration becomes slower and slower as the water swells the fibers in the paper and reduces the pore size. The greatest swelling takes place at the surface of the sheet where the fibers have been in contact with liquid for the longest time, thereby forming constrictions at the openings of the pores which reduce the amount of ink which can get through.

Sizing against Coarse Suspensions

In coarse dispersions where the particles in the penetrating fluid are very large in size, there may be a mechanical retarding of penetration by a "filtering-out" effect. This effect is important with certain printing inks, impregnants, and similar materials where the dispersed particles are coagulated or filtered out at the openings of the pores of the paper. In the case of printing inks, this action often hinders further penetration of the vehicle into the paper.

The filtering out of coarsely suspended material on the surface of paper is dependent primarily upon the density or porosity of the paper, rather than upon the sizing value. It takes place when the vehicle is relatively free to penetrate into the paper, but the suspended material is too coarse to enter the pores of the paper.

Methods of Measuring Sizing

Many tests are used to measure sizing. A few of the more important tests are described below. These are, for the most part, empirical use tests, which are influenced by the area and thickness of the paper specimen. It is important, when describing how well sized a paper is, to mention the method of testing, since results differ, depending upon the test method used.

Cobb Size Test

The Cobb size test measures the amount of water absorbed by the paper in a given period of time. In this test, a circular metal ring (7.5 cm. high and usually 10 cm. inside diameter) is placed on a weighed sample of paper and then a carefully measured volume of water (usually 75 cc.) is added. After a definite period of time, the water is poured off and the sheet

is blotted with blotter or towel until the shine from the surface water is gone, after which the sheet is reweighed. The gain in weight is reported as the amount of water in grams which is absorbed by 100 sq. cm. of paper surface.

The Cobb size test works best for heavyweight papers (papers over 0.004 in. in thickness) which are fairly well sized. It is not recommended for testing the surface resistance of writing papers to ink or for the testing of papers which soak through in less than fifteen seconds. This test has been described in the literature,^{18, 19, 20} and typical results are shown in Figure X-2.

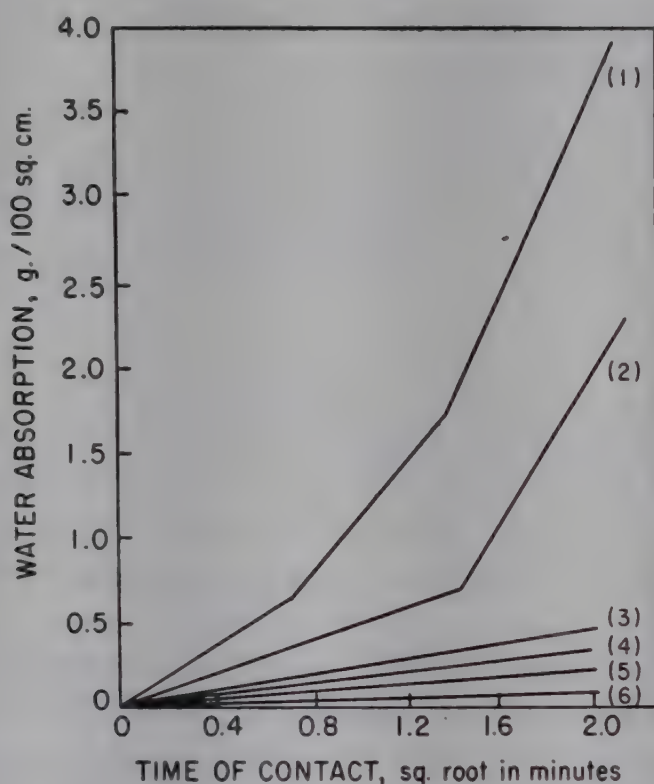


Fig. X-2. Sizing as measured by Cobb size test on different papers: (1) patent coated news (felt side); (2) same, wire side; (3) Kraft wrapper (wire side); (4) same, felt side; (5) manila; (6) ledger.

According to Codwise,²¹ the amount of water absorbed in the Cobb test varies directly as the square root of the time during which the water is in contact with the paper. For hard-sized papers, an exposure of 120 seconds is generally used, whereas a shorter period (e.g., 60 seconds) is better suited for soft-sized papers. If desired, a curve may be drawn, as in Figure X-2, showing the pick-up of water versus the time of exposure. For a universal test figure, the results can be plotted against the square root of the time of exposure and the curve extrapolated back to a time of one minute. Both the felt and wire sides of the paper should be tested. One

¹⁸ R. M. Cobb and D. V. Lowe, *Tech. Assoc. Papers* 17: 213-216 (1934)

¹⁹ R. M. Cobb, *Paper Trade J.* 100, No. 16: 200-203 (Apr. 18, 1935)

²⁰ P. W. Codwise, *Paper Trade J.* 102, No. 3: 39-43 (Jan. 16, 1936)

²¹ P. W. Codwise, *Paper Trade J.* 102, No. 3: 41-43 (Jan. 16, 1936)

advantage of this test is that the results are independent of sheet thickness. In grading papers for sizing by the Cobb test, hard-sized papers are considered as those which absorb less than 0.06 g. of water, whereas slack-sized papers are those which absorb 0.60 g. or more of water per 100 sq. cm.

Carson Curl Test

In the Carson curl test, a strip of paper is wetted on one side with water, and notation made of the maximum curl of the paper and the time required to reach the maximum curl. The maximum curl is a measure of the tendency of the paper to curl, whereas the time to reach maximum curl is a measure of the sizing value.

The time to reach maximum curl is determined by the time required for the water to penetrate halfway through the paper after it first comes into contact with the water. An approximate comparison between papers of different thicknesses can be obtained by dividing the time of curl by the square of the thickness.

Ink Flotation Test

In the ink flotation test, a sample of paper with the edges turned up is floated on a standard writing ink, and the time is taken for the ink to penetrate through the paper and discolor the surface. This test is rather unscientific because of the indefiniteness of the end-point which is left to the discretion of the tester, but the test is useful for measuring the resistance of paper to the penetration of writing inks and is widely used for that purpose. The test is also valuable for measuring the resistance of paper to other colloidal solutions aside from ink as, for example, blood. The test is, however, of relatively little value for measuring the resistance to water, and is therefore not suitable for testing hard-sized papers such as are used for food containers and drinking cup stock.

The end point of the ink flotation test depends to a slight degree upon which side (the felt or the wire side) of the paper is placed in contact with the ink. However, the results are not a satisfactory indication of the difference in writing qualities between the two sides of the sheet. A better test for this purpose is the "pen and ink" test, in which the paper is ruled with a standard ink and any tendency toward feathering is noted (see next chapter).

In one variation of the standard ink resistance test, the paper is allowed to remain in contact with the ink, felt side down, for a definite period of time, usually thirty minutes. At the end of this period the excess ink is blotted from the surface of the paper, and the wire side of the paper is rated visually for penetration of ink. If desired, a numerical reading can be obtained on a Bausch and Lomb opacimeter by first standardizing

the instrument at a reading of 50, using four sheets of the original uninked paper, and then taking a reading on the inked specimen with the uninked side toward the light.

Dry Indicator Test

In the dry indicator test, a finely ground dry indicator powder consisting of powdered sugar, soluble starch, and about 2% of methyl violet is dusted on one surface of the test sheet. The sheet is then floated on water, and the time is taken for the water to pass through the sheet and change the color of the indicator.

In this test, most of the water passes through the paper in the liquid state, although Carson²² and others²³ have pointed out that enough water may pass in the vapor state to change the color of the indicator. This susceptibility of indicator power to water vapor is a fundamental defect of this test.²⁴ However, with ordinary papers, Carson found that liquid water passes through the paper faster than water vapor, so that the end point of the test is probably not affected by the transmission of water vapor. With thick papers requiring long penetration periods, the results may be in error by several hundred per cent, because of the sensitivity of the indicator to water vapor.²³ The results are also affected by the amount of indicator powder shaken on the paper.

Conductivity Methods

There are several conductivity methods for measuring sizing based upon the rate of penetration of a conducting solution through a sample of paper. The most widely used of these testers is the Valley size tester. Recently a new electronic size tester has been described²⁵ which uses a saturated solution of calcium sulfate as the electrolyte solution.

In the Valley size tester, a sheet of paper (2 × 2 in.) is clamped in a cell between two electrodes which are part of a Wheatstone bridge. The cells have inlets connected by means of rubber tubing to bottles of electrolyte solution. When the cells are lowered, the solution runs into the cells, and a closed circuit is made immediately if there is no paper present. If a specimen of paper is placed between the electrodes, no current will flow so long as the paper remains dry, but as soon as the electrolyte solution penetrates the paper, current is built up and this registers on an ammeter in the circuit. In making the test, the rheostats in the circuit are set so that the

²² F. T. Carson, *Paper Trade J.* 98, No. 21: 264-266 (May 24, 1934)

²³ P. E. Marenholtz, *Tappi* 33, No. 6: 289-291 (June, 1950)

²⁴ W. A. Wink and J. A. Van den Akker, *Paper Trade J.* 125, No. 8: 86-90 (Aug. 21, 1947)

²⁵ F. W. Elliot, *Pulp Paper Mag. Canada* 50, No. 3: 125-128, Convention Issue (1949)

ammeter registers 200 ma. when the cells are full and no paper is present. When the sample of paper is tested, the end point is taken as the time for the current to build up to 160 ma. (since the current will never read 200 ma. with the paper present). The results are affected by the degree of sizing of the paper, porosity, thickness of paper, temperature of electrolyte solution, and other similar factors.

Wet Break Test

One of the newer tests used successfully in some mills is the wet break test. This test not only measures the degree of sizing and but also measures the wet strength of paper.

When the wet break test is used for measuring sizing, weights are fastened to strips of paper held in a vertical position and the paper is immersed in water, or any other test fluid desired. The time required for the strip to break is taken as a measure of the degree of sizing. This test gives a good end point, and the human element is at a minimum. When the test is made with different weights and different periods of test time, it furnishes considerable information on the sizing properties of the paper.²⁶

According to Wilson,²⁷ results of the wet break test, unlike those of the dry indicator test, increase appreciably when the amount of rosin size added to the paper is increased. He found that the wet break test agrees very closely with the equilibrium water pick-up of the paper.

Penescope Test

The water resistance of paperboard is sometimes measured in the penescope. The penescope consists of a brass chamber fitted with an upright piece of glass tubing and a hollow screw cap which forms an open face through which the specimen can be observed. In testing, the specimen of paper is cut in a circular form and placed in the inside of the screw cap and screwed into place across the face of the brass chamber. The chamber is filled with the test liquid and excess liquid added until it rises in the glass tubing to a height of 1 ft. At this point, a stopwatch is started, and the time is taken until the end point of the test is reached.

The test liquid is usually lactic acid solution, which is a faster penetrating agent than water. The board is first painted with methyl orange on the outside surface, and after the methyl orange has dried, the time is taken for lactic acid to penetrate the board and produce five red spots on the outside surface of the board. The end point of the test is affected by the concentration of the acid solution,²⁸ and normally, a 10% solution of acid is used. The temperature of the solution and the hydrostatic head also affect the end

²⁶ W. S. Wilson, *Paper Trade J.* 128, No. 5: 40-44 (Feb. 3, 1949)

²⁷ W. S. Wilson, *Paper Ind.* 30, No. 10: 1514-1522 (Jan., 1949)

²⁸ C. E. Libby and F. Casciani, *Paper Trade J.* 94, No. 20: 260-263 (May 19, 1932)

results. Water may be used as the test liquid, in which case the pick-up of water is determined by weighing the sample before and after the test.

Soak Tests

Some board mills use a soak test to measure the water resistance of paperboard. In this test, a sample of board of definite size is weighed and then immersed in water, where it is left for a definite time (usually 10 minutes). At the end of this period, the sample is removed, all surface water is removed by blotting, and the sample is reweighed. The gain in weight is reported as the sizing value. Wilson²⁷ found that the ratio of water picked up varies with the sheet weight, and that approximately one hour's time is required to reach a practical equilibrium.

Ulm²⁹ used a buoyancy test for measuring sizing. He found that hard-sized papers retain their buoyancy, whereas slack-sized papers became less buoyant on soaking in water. The reason that hard-sized papers retain their buoyancy is that they absorb very little water. In comparison, slack-sized papers absorb considerable water, and this absorption of water displaces air in the paper, resulting in a loss in buoyancy.

The loss in bursting strength which results when paperboard is soaked in water or floated on the surface of water is sometimes used as an indication of the degree of sizing. However, this test is of no value as an indication of sizing if the paperboard has been treated with special agents for increasing the wet strength.

Angle of Contact Test

One of the most important fundamental tests for measuring the surface resistance of paper to water and aqueous liquids is the test used for measuring the angle of contact formed when a drop of water or other test liquid is applied to the surface of the paper. Two different values may be obtained in this test, an initial wettability and a rate of change of wettability.

The initial wettability, which is a measure of the ruling and writing qualities of the paper, is obtained by taking a reading of the contact angle five seconds after the drop of water has contacted the paper. Excellent ruling and writing qualities prevail when this initial angle of contact (with water) lies between 100 to 90°. When the angle is greater than 110°, breaks in the ruling line are likely to occur because of poor wetting. When the angle is smaller than 90°, the ink line is likely to feather as soon as the ink contacts the paper surface.

The rate of change of wettability, which is also a measure of writing quality inasmuch as it directly measures the tendency of the paper toward feathering, is obtained by subtracting the angle of contact obtained after

²⁹ R. W. K. Ulm, *Paper Trade J.* 119, No. 9: 87-88 (Aug. 31, 1944)

sixty seconds has elapsed from the reading obtained after five seconds and dividing the result by 55. When writing upon papers of medium sizing, feathering often does not occur until a short time has elapsed, during which the ink had had a chance to penetrate the paper. Such a tendency will be indicated by a decrease in the angle of contact between the five-second and the sixty-second reading. Hard-sized papers will show no perceptible change between these two readings.

The angle of contact is measured in a special apparatus. Test specimens of paper are placed upon a stage and held in place by means of weights. A drop of water ($\frac{1}{150}$ – $\frac{1}{200}$ ml.) is placed on the paper by means of a hypodermic needle held $\frac{1}{8}$ in. from the surface of the paper and the image of this drop, enlarged 25 to 30 times, is then projected on a frosted glass screen at the back of which is clamped a sheet of transparent onion skin paper. A horizontal line is drawn on the transparent paper to indicate the base of the drop, and then as soon as the required time has elapsed, two tangents are quickly drawn to the curve of the drop at the two points of contact with the base line. The interior angle which these tangents make with the inside base line is the angle of contact.

The results of the surface wettability or contact angle test depend upon the following factors: the wetting power of the solution, the wetting properties of the sizing agent, and the surface texture or finish of the paper. Sometimes the liquid does not uniformly wet the paper at first. This is the

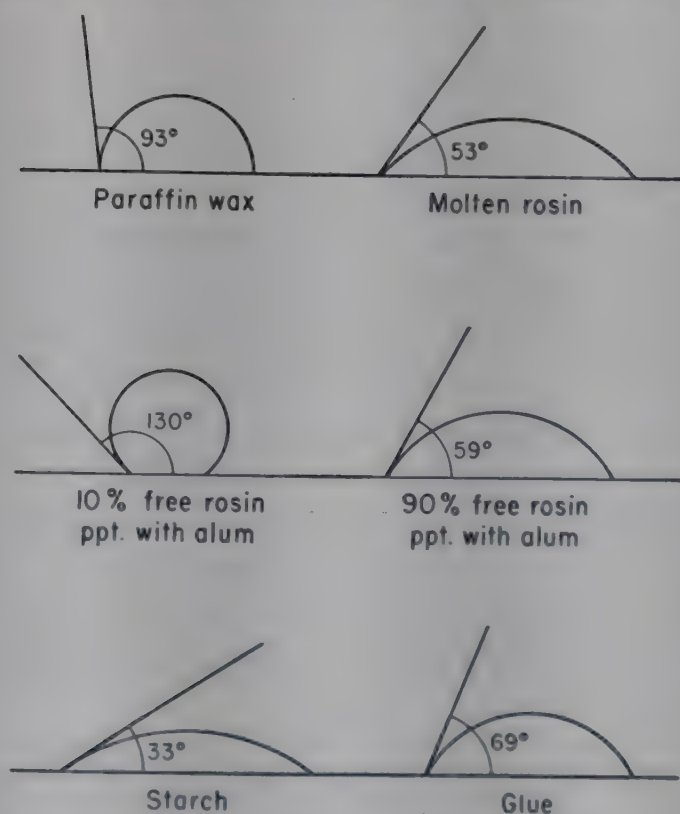


Fig. X-3. Angles of contact formed by a drop of water on films of different sizing agents.

result of either lack of uniformity in pore structure of the paper, non-uniform distribution of sizing agent resulting in a variation of contact angle from point to point on the paper, or unevenness in the surface finish of the paper.

Lafontaine³⁰ has measured the angles of contact formed by drops of water on films of different sizing agents used in paper making. His results, which are illustrated in Figure X-3, show that paraffin is more water repellent than rosin, and that the type of rosin size used has an appreciable influence on the water repellency of the precipitate. The surface-sizing agents (starch and glue) are definitely lower in water repellency than either paraffin or rosin. The presence of materials such as clay in the paper tends to decrease the contact angle and lower the sizing value.

Tests for Absorbency

Most commercial papers require some degree of resistance to the penetration of liquids, and hence most commercial papers are sized. There are, however, a few grades of paper which require a high degree of absorption for liquids. These are known as absorbent papers, and some of the important commercial grades are blotting papers, filter papers, sanitary tissue, and paper toweling. Papers to be treated with special chemicals, such as vulcanized paper and vegetable parchment, also fall in this class. All these papers are related because they are unsized, or waterleaf, and are made in a soft, loosely felted condition in order to obtain maximum absorbency.

Toweling and tissue must have a high degree of absorbency in order to take up water quickly and hold it after absorption. In addition, these grades must have a high degree of softness. In order to obtain these qualities, the stock for toweling and tissue is unsized and usually beaten only lightly, if at all. Very often the sheet is creped, because this increases both the softness and the absorbency.

Soft rags or high alpha pulps are generally used in the manufacture of the highest grades of absorbent paper, since these pulps produce the most porous papers. In the medium grades, mixed furnishes of rag and sulfite may be used, and in some cases, up to 100% chemical wood pulp, such as unbleached sulfite or a mixture of sulfite and soda, is used. In the lower grades of toweling, groundwood is frequently used. During the drying of absorbent papers, care must be taken to prevent case hardening of the surface fibers, inasmuch as this reduces the absorbency of the sheet.

In many cases it is desirable to measure the absorptiveness of paper, and consequently several tests have been devised to measure this property. Among these tests are the following:

(1) A pipette test in which a stated amount of test fluid is flowed onto a small sample of paper and the time is taken for the complete absorption of the fluid, as evi-

³⁰ G. H. Lafontaine, *Paper Trade J.* 113, No. 6: 63-65 (Aug. 7, 1941)

denced by the disappearance of the glossy, liquid surface. The test liquid may be ink (for testing blotting papers) or water (for testing toweling).

(2) A strip method whereby a strip of the specimen is hung so that one end is suspended in the test liquid. The end point can be taken as (a) the time for the liquid to rise to a given height or (b) the height of rise of the liquid in a given period of time.

(3) A dip test in which a small weighed specimen of the paper is dipped into the liquid with which it is to be saturated and the weight of absorbed material is measured after a given period of time. In testing heavy boards, it is advisable to seal off the edges of the sample, since the rate of absorption is generally different from the edges than it is from the top or bottom of the board.

Internal Sizing with Rosin

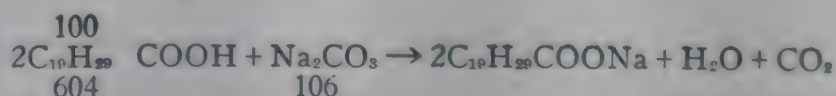
Rosin size is made by cooking rosin and alkali in either an open or a pressure cooker to produce a product containing varying amounts of "free" rosin, depending upon the degree of saponification of the rosin by the alkali. In the past, many paper mills prepared their own rosin size in cookers of various design, but the batches were small and there was relatively little control of the reaction. Today, a large majority of the mills use prepared size produced in large, uniform batches by the chemical companies. These prepared sizes, which are sold as paste rosin size or as dry rosin size, require only dilution with water before use. They are ordinarily very uniform with respect to grade of rosin, free rosin content, free alkali, per cent solids, and viscosity.

Dispersion of Rosin with Alkali

Rosin size is generally made by the saponification of rosin with sodium carbonate or sodium hydroxide. In making the size, the alkali and rosin are heated together. During the heating the alkali reacts with the rosin in various proportions, depending upon the amount of alkali used, temperature, and time of boiling.

Sodium carbonate is the alkali generally used for the preparation of commercial size. In one method of manufacture, the rosin is first melted, sodium carbonate is then added in the form of a solution, and the mixture is heated for two to seven hours. In other cases, the rosin is added to a boiling solution of sodium carbonate. Carbon dioxide is given off as long as the reaction proceeds.

The theoretical amount of sodium carbonate required to obtain a fully saponified size is approximately 17.5% sodium carbonate for pure abietic acid, as shown by the equation below:



$$\text{amount of sodium carbonate} = (100 \times 106) / 604 = 17.5$$

However, abietic acid is only one of the components of rosin, and hence the

acid number of the particular rosin in use must be known to determine the theoretical amount of alkali required for that rosin. If the acid number of the rosin is known, the results obtained from the above equation can be multiplied by a factor obtained by dividing the acid number of the rosin by the acid number of abietic acid (186). If a partially saponified size is desired, this value should be multiplied by the percentage of saponified rosin desired in the size. These relationships are only theoretical, and it should be pointed out that the amount of alkali to obtain an equivalent size in commercial operation may be different from that indicated by the above calculations.

Ammonia is a very rapid solvent for rosin, but it has never been widely used. Ammonia resinate has been suggested,³² however, for the sizing of papers containing alkaline fillers where regular rosin size is not satisfactory. Ammonium resinate is effective under these conditions, since it is supposedly decomposed by the heat of the driers, thus liberating rosin.

Sodium hydroxide can be used as the alkali for making rosin size. The rate and degree of reaction is much greater than it is with sodium carbonate, and even dilute solutions of sodium hydroxide dissolve rosin in the cold, giving almost complete saponification. This reaction is the basis of a commercial process which will be discussed later.

When preparing free rosin size, part of the rosin is converted into sodium resinate and passes into true solution, while the remaining part of the rosin is colloiddally dispersed as free rosin. This free rosin is stabilized by the presence of the resinate, and there is an optimum ratio of saponified rosin to free rosin which gives the most stable dispersion. If too little saponified rosin is present, the electrostatic charges on the dispersed particles will be insufficient to maintain a stable dispersion.

Analysis of Rosin Size

The important characteristics of rosin size are total solids content, free rosin content, and alkalinity. If any of these properties is found to be abnormal, the chemist should check with the supplier, or if the size is prepared at the mill, a check should be made on the method of preparation.

If the rosin size is prepared at the mill, some of the important factors are: saponification number of the rosin, amount of alkali used in saponification, amount of water used, temperature and time of cooking, temperature and rate of emulsifying, and composition of dilution water.

The following methods of testing apply to rosin paste, which is a viscous dispersion of rosin size normally containing 70% dry solids, but which can be obtained in solids content ranging from 50 to 80%. There are separate methods for the analysis of dry rosin size and rosin size emulsion. These procedures are described in TAPPI Standards (T628 m-43).

The total rosin content in rosin size paste can be determined by the amount of material extracted with diethyl ether, when the rosin paste is shaken with water, acid and ether. •

The amount of free rosin can be determined either by titration or by extraction. In the titration method, the rosin is dissolved in anhydrous isopropyl alcohol and titrated in the presence of thymol blue with 0.5 *N* alcoholic (isopropyl) potassium hydroxide, using monochromatic light from a special filter. In the extraction method, the rosin is dissolved in a mixture of neutral ethyl alcohol and water and then extracted with ether. The weight of ether extract is then obtained and reported as the free rosin.

The amount of combined rosin is calculated as the difference between the total rosin and the free rosin.

The amount of unsaponifiable material is obtained by first treating the rosin with 0.5 *N* alcoholic potassium hydroxide and then extracting the unsaponifiable matter with ether.

If wax is present, it can be determined by the difference between the total solids and total rosin size content of the size but this is not very satisfactory. A much better method is one which is based upon the high solubility of wax in hot acetic anhydride³¹ and its insolubility in cold acetic anhydride.

Neutral Rosin Size

Neutral rosin size is size in which the rosin acids are entirely combined with alkali. In other words, the reaction, rosin acids + alkali \rightarrow sodium resinate, has gone to completion, and there are no free rosin acids left in the mixture. Neutral size is very soluble and forms a clear solution. It forms rigid gels in concentrated solutions.

There are several processes for preparing neutral rosin size. One of these is the Delthirna size process which, although not so widely used as it has been in the past, serves to illustrate one method of preparing neutral size. In this process, a cold solution of sodium hydroxide flows through large tubes filled with coarsely ground rosin. The size is removed at the other end of the tubes in the form of sodium resinate. It is claimed that each particle of size exists in the molecular state,³² and that this is the reason for the effectiveness of this size when precipitated in the beater. This type of size seems to have some advantage in the sizing of groundwood papers because of the extra alkali in the size which disperses the resins in the groundwood and results in an additional sizing effect from these resins.

A convenient source of neutral rosin size is a commercial product known as dry rosin size, which is a highly saponified rosin soap sold in powder form. The product is highly soluble and dissolves readily in cold water, so that it may be added to the beaters either after dissolving in water

³¹ W. E. Shaefer and A. C. Dreshfield, *Paper Trade J.* 111, No. 20: 249-251 (Nov. 14, 1940)

³² J. A. De Cew, *Paper Trade J.* 100, No. 11: 144-146 (Mar. 14, 1935)

³³ R. Hilaire, *Paper Trade J.* 91, No. 2: 21-22 (July 12, 1930)

or in the dry state. The development of dry rosin size was held up for many years because of the storage difficulties arising from the oxidation of the rosin. This difficulty has been overcome by the addition of anti-oxidants, so that a good grade of dry rosin size is available today. There are many patents on methods of making dry rosin size. Some methods call for grinding rosin and alkali together,³⁴ others for spraying alkali into rosin,³⁵ and still others for spray-drying the reaction mixture of alkali and rosin.³⁶

Free Rosin Size

The amount of free rosin in commercial size preparations varies all the way from a fraction of 1% to a high percentage of the total solids, depending upon the method of preparation. The highest percentage of free rosin in commercial paste rosin size is generally about 30% as determined by titration, or roughly 40% as determined by extraction.

High free rosin size is more difficult to handle than neutral size, and would not be used except that it produces better results under some mill conditions. The relative merits of high free rosin size and low free rosin size has been a controversial subject for many years, but it is now pretty generally recognized that high free rosin size results in better sizing and uses less alum. Lafontaine³⁷ found that papers sized with high free rosin size have a higher surface wettability (lower contact angle) than papers made with low free rosin size, but on the other hand, have a higher water resistance. He suggests that writing papers which are not subsequently surface sized with starch or glue might advantageously be sized with low free rosin size, whereas such grades as wrapping paper, which require a high resistance to water penetration, might be sized most advantageously with high free rosin size.

Dilution and Emulsification of Rosin Size

Neutral rosin size and rosin size containing a small percentage of free rosin can be readily diluted with water. In some cases, neutral rosin size can be added directly to the papermaking stock without dilution. On the other hand, emulsification of the size is necessary with high free rosin paste size and is desirable even with low free rosin paste size, since it produces better sizing and results in more trouble-free operation.

Many mills use dilute emulsions of rosin size in a range of concentration of 2 to 5% prepared from rosin size containing up to 30% free rosin.

³⁴ M. Engelmann, U. S. 2,052,170 (Aug. 25, 1936)

³⁵ W. H. Harding, U. S. 2,128,482 (Aug. 30, 1938)

³⁶ A. C. Dreshfield and H. A. Johnstone, U. S. 2,134,911 and U. S. 2,134,912 (Nov. 1, 1938)

³⁷ G. H. Lafontaine, *Paper Trade J.* 113, No. 6: 63-65 (Aug. 7, 1941)

This diluted size is somewhat less stable than concentrated size because dilution reduces the stabilizing effect of the sodium resinate on the unsaponified rosin,³⁸ but when properly emulsified, size of good stability can be prepared in this range of concentration. However, if dilution of the size is carried too far, coagulation of the dispersed rosin occurs and the effectiveness of the size is reduced. The color of emulsified size varies from a clear emulsion to a milky emulsion, depending upon the conditions of emulsification. Some mills prefer a milky emulsion and others a clear emulsion, but in general, the clearer the size, the finer the dispersed particles and the more stable the size. A bluish fluorescence indicates a highly dispersed condition.

The difficulties in handling high free rosin size can be eliminated by using special emulsifying apparatus. A continuous, automatically controlled process for emulsifying rosin size paste has been developed to replace the older batch process.^{39, 40, 41} The principles of emulsification are the same as those in the batch process, but the automatic operation provides a nearly continuous supply of emulsified size. In this process, the three components necessary for emulsification, rosin size, hot water, and cold water, are delivered at the proper rate by means of three proportioning pumps driven by a single motor. The thick paste size flows from a storage tank through a heat exchanger where the temperature is brought to the proper point. The heated size is then pumped to an ejector where it is combined through Venturi sections with hot water from the second pump. This primary emulsion then flows through a turbine mixer (a cylindrical chamber containing a spiral rotating baffle) where further mixing of the size takes place. Finally the emulsion is diluted in a storage tank with cold water from the third pump to a concentration of about 4 to 5%. Size emulsion can be drawn from this tank as needed.

Even under the best conditions, dilute emulsions of free rosin size are relatively unstable and must not be stored for long periods, particularly if stored at high temperatures. The stability of the emulsion depends upon the emulsifying conditions, the amount of free rosin, amount of total alkali, and to a lesser extent upon the amount of free alkali. The type of water used for dilution is another important factor. For best results, softened water or condensed steam should be used for diluting size, but most mills use regular mill water. Unusually hard water causes trouble.

Protected Rosin Size

By using a protective colloid, it is possible to prepare highly stable size

³⁸ C. C. Irving, *Paper Mill* 62, No. 45: 18, 20-21 (Nov. 11, 1939)

³⁹ *Paper Ind.* 30, No. 10: 1453-1454 (Jan., 1949)

⁴⁰ *Pulp and Paper* 23, No. 2: 53-54 (Feb., 1949)

⁴¹ Process developed by Hercules Powder Company, Wilmington, Del.

containing as high as 90% free rosin. The process consists of two steps: preparing the rosin in a state of fine subdivision and adding a protective colloid to prevent further growth of the rosin particles.

The use of protective colloids for stabilizing rosin size is not a new principle, since the rosin soap present in free rosin size may be regarded as a protective colloid. Furthermore, it has been common practice among papermakers to add protective colloids, such as oxidized starch, casein, soybean protein, and animal glue, to the papermaking stock in the beaters before the rosin size is added, particularly where hard water is used. However results are better if protected size is prepared as a mixture under conditions which control the relative amounts of free and combined rosin and the size of the free rosin particles. These protected sizes can be prepared in the paper mill (Bewoid or Prosize process), or protected size may be purchased in prepared form at concentrations from 40 to 50%.

Protected size has several advantages over ordinary free rosin size. Most of the size exists as free rosin, and hence, calcium and magnesium ions or excessive acidity in the beater do not interfere with the sizing. Another advantage of protected size is that no special precautions are necessary in diluting or handling the size, since properly prepared protected sizes do not form rosin spots when added to the stock in an undiluted state. However, the efficiency is increased if they are diluted before being added to the beater. There are two important commercial processes for preparing protective size, the Bewoid and the Prosize processes.

Bewoid Process. The Bewoid process is a patented process for preparing high free protected size in the paper mill. Bewoid size, as usually prepared, contains about 90% free rosin dispersed in a small amount of rosin soap and stabilized by the presence of about 2% casein or other protein on the weight of the rosin.

The Bewoid process involves the mechanical subdivision of rosin in the presence of about 1 to 2% sodium hydroxide and about 2% casein. The rosin is heated and subjected to mechanical shearing stress until it is subdivided into small particles. A small amount of caustic soda (1.6 parts per 100 parts of rosin) is then added to the melted rosin to saponify part of it, and then casein (2.0 parts casein dispersed in 0.2 part caustic) is added to stabilize the dispersed particles of rosin. The dissolved casein is run into the molten rosin under vigorous agitation, after which an additional small amount of caustic (0.2 part) is added. Water is finally added to produce a finished dispersion containing about 45% solids.

In prepared Bewoid size, the particles of dispersed rosin show a polydispersoid ball structure which range from 0.5 to 2.0 microns in size,⁴² and have an average size of about 1.0 micron. Photomicrographs of Bewoid

⁴² B. Wieger, *Paper Trade J.* 101, No. 5: 51-54 (Aug. 1, 1935)

size have been taken after coagulation which show that the floc obtained with Bewoid size is quite different from that obtained with unprotected size.

Mashburn⁴³ has patented a somewhat different process in which a non-alkaline dispersing agent (sulfonated higher fatty alcohol) is used in place of sodium hydroxide. The rosin and organic dispersing agents are melted together and a protein is added as a protective colloid. The advantages claimed are a reduced amount of alum required for precipitation and the elimination of salt as a by-product of the sizing reaction.

Prosize Process. The Prosize process is another patented process which can be used in the paper mill to produce protected size containing a high free rosin content. The Prosize process usually starts with a solution of paste size containing 12 to 20% free rosin which is subsequently converted by the action of acidic materials into a size of much higher free rosin content. The rosin particles are condensed from a supersaturated state of molecular subdivision into larger and larger particles, until the growth is arrested and the particles prevented from growing into larger aggregates by the presence of a surface-active protein. Soybean protein is the protein generally employed, although other proteins may be used. The protein serves not only to arrest the growth of the rosin particles, but also to stabilize the resulting sol by forming an interfacial film around the rosin particles.

In preparing Prosize, dry soybean protein is added to a solution of sodium resinate, followed by the addition of boric acid. The protein, because of its acidic nature, forces the hydrolysis of the resinate into free rosin by removing alkali from the sodium resinate. The boric acid completes the hydrolysis started by the protein. According to Rowland,⁴⁴ the use of protein alone gives larger rosin particles than those produced with boric acid because of the longer time required for reaction. However, protein must be used not so much to initiate the hydrolysis, but more importantly, to limit the growth of the rosin particles and to stabilize the final emulsion.

Size obtained by the Prosize process contains finely divided rosin particles, some of which are in the ultramicroscopic range.⁴⁵ The particle size depends to a large extent upon the temperature used in preparing the size. The rosin particles are enveloped in a protecting film of protein which causes the rosin particles to act more nearly like protein particles than rosin particles; that is, they have the isoelectric point and electrophoretic behavior of soybean protein, rather than that of rosin.

⁴³ R. T. Mashburn, U. S. 2,393,179 (Jan. 15, 1946)

⁴⁴ R. W. Rowland and W. M. Bain, *Paper Trade J.* 110, No. 17: 237-240 (Apr. 25, 1940)

⁴⁵ R. W. Rowland and W. M. Bain, *Paper Trade J.* 110, No. 17: 237-240 (Apr. 25, 1940)

Amount of Sizing Agent Used

The amount of rosin size used in the sizing of paper depends upon the functional requirements of the paper and the efficiency obtained from the size. The amount varies from 0% size in absorbent papers to about 5% size in certain speciality papers and paperboards. The approximate amounts of rosin size used in a few different grades of paper are given in Table I.

TABLE I
AMOUNT OF ROSIN SIZE USED IN COMMERCIAL PAPERS

Paper grade	Amount of rosin size generally used, %
Newsprint	0 (sometimes 0.5)
Bond paper	1.0-2.0
Ledger paper	1.5-2.5
Book paper	0.5-2.0
Mimeograph	1.0
Coating rawstock	0.5-1.5
Blueprint and direct process	2.5-5.0
Cover paper	2.0
Envelope	1.5-2.5
Hanging paper	2.0-2.5
Bottle-cap board	3.0-4.0
Patent coated board (frequently only the liner is sized)	1.0-2.0

The sizing value does not increase in direct proportion to the amount of sizing agent added, even in the commercial range. The greatest increase per increment of added size is generally obtained in a range of about 0.75 to 1.5% size on the weight of the pulp. The efficiency then decreases with higher percentages of size up to about 2 to 3% size, depending upon the type of pulp and mill conditions, after which further addition of size results in greatly reduced efficiency. However, some grades of paper are customarily made with greater amounts of size than this, as shown in Table I. In these grades, extra size is needed to obtain the results desired, even though the efficiency of this extra size is rather low. As already shown in Figure X-1, the results depend upon whether water or ink resistance is desired, since ink resistance normally increases with increasing rosin size long after the water resistance test has begun to show very little further improvement.

The amount of rosin in paper can be determined both qualitatively and quantitatively by means of suitable tests. The Liebermann-Storch test and the Raspail test are qualitative tests. In the Liebermann-Storch test, a small piece of paper is placed in a test tube, covered with acetic anhydride, and boiled down. The liquid residue is

then placed in a porcelain crucible and a small drop of concentrated sulfuric acid run down the side of the crucible into the liquid residue. A fugitive rose-violet coloration where the acid meets the anhydride indicates the present of rosin in the paper. In the Raspail test, a drop of concentrated sulfuric acid is added to the paper after it has been treated with a drop of saturated sugar solution. A raspberry red coloration developed by the acid is indicative of rosin.

In testing for rosin quantitatively, the paper is first extracted with an alcohol-acid mixture. Then, the rosin is separated from the non-resinous materials in the alcohol-acid extract by shaking the extract with dry ether. Evaporation of the ether-soluble material gives the dry weight of rosin in the paper.

Precipitation of Rosin Size with Alum

In order to obtain the desired results from rosin size, it must be precipitated in the papermaking stock with alum. Unless alum is added, the rosin size will be washed out of the sheet. Acids, acid salts, or the salts of alkaline earth metals can be used in place of alum for precipitating rosin size, but the sizing is not so good nor so permanent as that obtained with alum.

Because of its almost universal use as a precipitating agent for rosin size, alum is of very great importance in sizing. The formula for papermakers' alum (which is not a true alum at all, since it is not a double salt) is generally represented as $\text{Al}_2(\text{SO}_4)_3$. Commercial alum, however, contains an excess of Al_2O_3 over the theoretical formula and is slightly basic. It also contains approximately 14.5 molecules of water of crystallization.

Alum is made from bauxite ore (a naturally occurring hydrous oxide of aluminum) by pulverizing the ore and reacting with sulfuric acid in lead-lined tanks. This forms aluminum sulfate which is decanted from the sludge (silica and other materials) and crystallized and sold in granulated, powdered, or slab form (or, in some cases, liquid form). Alum can be made in the paper mill (Kamig process) by reacting sulfuric acid with clay, but this process has the disadvantage that part of the non-soluble residues are left in the alum and added to the pulp. Most commercial alum used in

TABLE II

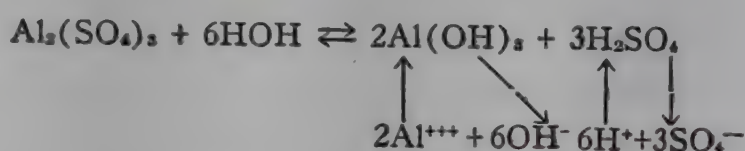
APPROXIMATE ANALYSIS OF COMMERCIAL GRANULATED ALUM

Total Al_2O_3	17.2%
Combined Al_2O_3	16.5%
Basic Al_2O_3	0.7%
Insoluble	0.07%
Fe_2O_3	0.01%
FeO	0.35%

papermaking is purchased in granulated form and has the approximate analysis given in Table II. Slab alum has less Al_2O_3 (15.5–16.0%) than that indicated in the table because high alumina content results in a fragile,

brittle slab. The iron content (expressed as Fe_2O_3) of alum must be below about 1.0% for newsprint and about 0.3% for writing and book papers, and the iron must be essentially all in the ferrous state. These requirements are ordinarily met by regular commercial papermakers' alum, but for special papers (e.g., high rag content papers and photosensitive reproduction papers), a special iron-free alum must be used. This alum, which contains only 0.01% Fe_2O_3 and no FeO , is made by dissolving aluminum hydrate in an iron-free grade of sulfuric acid.

Alum is generally dissolved in water before adding to the papermaking stock containing the rosin size. When dissolved in water, hydrolysis occurs as follows:



Since the ionization of sulfuric acid is greater than that of aluminum hydroxide, the final solution is definitely acid and generally buffers around a pH of 4.0, although pH values as low as 2.5 may be obtained. This acidity of alum serves to acidify the sodium resinate present in the size and to neutralize any alkaline materials in the pulp and water suspension. The important points to consider so far as the composition of the alum solution is concerned are total solids content, pH value, total acidity, and alumina content (see TAPPI Standards). Steps should be taken to control these variables in case any appreciable fluctuations occur.

The amount of alum used to set rosin size depends upon the amount of size used, the character of the stock being sized, the character of the water, and the amount of reused water. In practice, about 1.5 to 2.0 parts of alum per part of rosin size are required to obtain proper sizing, although the theoretical amount of alum required to react with rosin size is far below

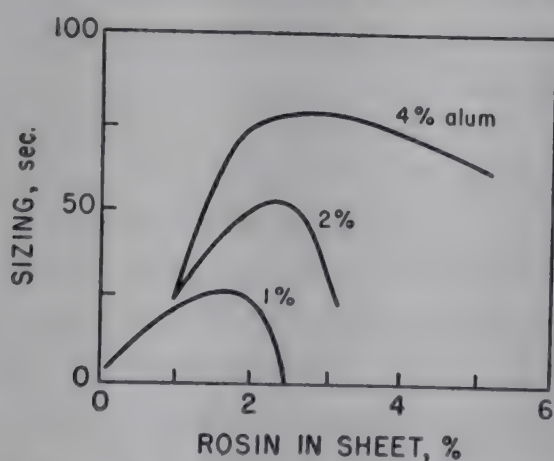


Fig. X-4. Effect of alum (percentage on curves) on ink resistance in papers containing different amounts of rosin.

this (about 0.37 part of alum per part of rosin size). This fact indicates that more than a simple chemical reaction between rosin size and alum is involved. The results of Wilson and Duston,⁴⁶ reproduced in Figure X-4, show that the ink resistance tends to increase as the amount of alum in the furnish is increased from 1 to 4% when the per cent rosin (as rosin) in the paper is varied from 0 to 6%. These results show that a high percentage of rosin size is valueless unless there is sufficient alum to react with the size. When highly sized paper is made, foaming may occur and the sheet may stick on the press; these troubles can often be overcome by adding more alum. The use of alum alone in groundwood furnishes can result in some ink and water resistance when the pulp has a high resin content.⁴⁷

The mechanism by which alum "sets" rosin size is highly important to the paper chemist, but unfortunately, it is a highly controversial subject which is not well understood. The literature is quite cluttered with contradictory findings, and in spite of the tremendous amount of research work which has been done on the subject of sizing, scientists, both individually and collectively, have not as yet arrived at a generally accepted theory, much less proved the exact mechanism of sizing. One of the reasons for this is that much of the information reported in the literature has been based on laboratory work obtained under a wide range of conditions which often were not well controlled. A further point to consider is that many of the findings obtained on the basis of laboratory work are not always reproducible in commercial operations.

One of the obvious roles of alum in sizing is to precipitate the rosin size, but considerable controversy has arisen over the nature of the rosin size precipitate. At the time of his discovery of rosin sizing in 1807, Illig believed that the rosin size was precipitated as free rosin and that this free rosin, as such, was the active sizing agent. Since that time, other investigators have proposed that the active sizing agent is not free rosin, but aluminum resinate, while still others have maintained that both free rosin and aluminum resinate must be present to obtain satisfactory sizing. Work by Price⁴⁸ on the study of rosin size precipitates obtained under various conditions has shown that the chemical composition of these precipitates can vary over a wide range without affecting the sizing efficiency. A material of the composition of aluminum diresinate, $\text{Al}(\text{C}_{20}\text{H}_{29}\text{O}_2)_2\text{OH}$, was found in papers sized with standard rosin size. In addition, free rosin was also present in the precipitate to the extent of that initially present, plus that formed by the reaction between sodium resinate and alum.

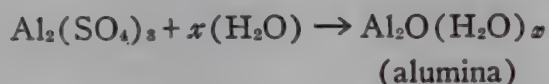
⁴⁶ W. S. Wilson and H. E. Duston, *Paper Trade J.* 117, No. 21: 223-228 (Nov. 18, 1943)

⁴⁷ R. T. Wetmore and L. W. Dunphy, *Tappi* 32, No. 4: 150-154 (Apr., 1949)

⁴⁸ D. Price, *Paper Trade J.* 126, No. 15: 191-196 (Apr. 8, 1948)

In addition to its role in precipitating rosin size, alum might also be expected to be involved in some complex mechanism by which the rosin size precipitate is attached to the fibers. Many theories and variations of theories have been proposed to explain this mechanism, but in general, these may be summarized into two general theories, namely, the alumina theory and the aluminum ion theory, both of which are discussed below.

Alumina Theory of Sizing. Sieber,⁴⁹ Lorenz,⁵⁰ and Ostwald⁵¹ were among the first to explain sizing in terms of colloid chemistry. They believed that sizing is obtained as a result of the reaction between negatively charged rosin particles and positively charged colloidal aluminum hydroxide, i.e., alumina. According to this theory, alumina is formed by the hydrolysis of alum, as shown in the formula, and this alumina is attracted and held to the negatively charged fibers. In this way, the fibers take on a positive charge which is responsible for attracting and hold the negatively charged rosin particles.



Ostwald and Lorenz⁵¹ showed that the best sizing was obtained at the isoelectric point; too little alumina left the fibers and rosin particles negatively charged, whereas too much alumina made them positively charged, resulting in poor sizing in either case.

According to the above theory, sizing is unsatisfactory at pH values below about 4.0 to 4.3 because no alumina is formed at these low pH values.^{52, 53} Some alumina may be present at pH value up to 10, but under highly alkaline conditions, the alumina does not function as a fixing agent because of the stabilizing action of hydroxyl ions on the rosin particles. According to Martin and Willets,⁵⁴ all the alum added to a pulp furnish is adsorbed as alumina up to an addition of about 4% alum, but when 7% alum is added, only about one-half is adsorbed. Increased beating, increased stock dilution, and increased temperature are some of the factors which appear to favor the adsorption of alumina by cellulose fibers.

In general, anions tend to lower the positive charge on alumina, making it much less efficient as a go-between for the negatively charged rosin and the negatively charged cellulose fibers. Thus, the building up of sulfate ion in the white water system accounts for the lowering of the sizing value

⁴⁹ R. Sieber, *Paper Trade J.* 75, No. 15, 16, 17, 18 (1922)

⁵⁰ R. Lorenz, *Paper Trade J.* 78, No. 23: 61-66 (June 5, 1924). Translated from the German by B. L. Kassing

⁵¹ W. Ostwald and R. Lorenz, *Kolloid-Z.* 32: 119-137, 195-209 (1923)

⁵² H. T. S. Britton, *J. Soc. Chem. Ind.* 127: 120-147 (1926)

⁵³ H. T. S. Britton, *Ind. Chemist* 4: 49-52 (1928)

⁵⁴ S. W. Martin and W. R. Willets, *Paper Trade J.* 110, No. 8: 98-104 (Feb. 22, 1940)

which is experienced under mill conditions when the white water is re-circulated. On the other hand, some sulfate ion is necessary for good sizing in order to coagulate the positive rosin-alumina complex on the fibers.⁵⁵ Thus, part of the effect of alum, in addition to its primary role of producing alumina, is to furnish sulfate ions for the coagulation of the alumina. Alumina by itself, in the absence of rosin size, imparts some sizing to the paper,⁵⁵⁻⁵⁷ although the effect is very slight.

Aluminum Ion Theory of Sizing. According to work by Price,⁵⁸ alumina, as such, is not part of the regular size precipitate. Alumina may be formed by the reaction of excess alkali in the system with alum, and alumina may even be coprecipitated with the rosin, but this alumina apparently has no beneficial effect on the sizing, and when present in excess, may reduce the sheet strength and lower the sizing.⁵⁹ As further evidence that alumina is not the active fixing agent, it has been pointed out⁶⁰ that the greatest amount of alumina floc from alum is obtained at a different pH value from which optimum sizing is obtained. In other words, the greatest amount of alumina is formed at a pH around 6, whereas the highest sizing is usually obtained in the pH range of 4.5 to 5.5. Thus, it would appear that alumina is not the agent responsible for the fixing of rosin size precipitate.

A theory held by many chemists is that the active "bonding" agent for fixing the rosin size precipitate on the fibers is not alumina, but aluminum ion. Wilson⁶¹ explains the role of aluminum ion by regarding pulp and rosin as ion exchangers whose surface cations are exchangeable with aluminum ions. It has been shown,⁶² in the case of pulp fibers containing calcium, that treatment with alum solution causes the calcium ions on the fibers to be replaced with aluminum ions in an ion exchange reaction. In the case of sized papers, aluminum ions are believed to be shared by both the rosin precipitate and the fiber, thereby acting as a mutual bonding agent between the two. According to this theory, rosin is easily saturated with aluminum ions, but pulp fibers are not readily saturated unless the aluminum ion concentration is quite high, thereby explaining the greater than stoichiometric amount of alum which is required in sizing.

⁵⁵ J. C. Redd, *Paper Trade J.* 119, No. 7: 66-71 (Aug. 17, 1944)

⁵⁶ W. Ostwald and R. Lorenz, *Kolloid-Z.* 32: 119-137, 195-209 (1923)

⁵⁷ B. W. Rowland and J. J. Harrison, *Paper Trade J.* 119, No. 20: 199-203 (Nov. 16, 1944)

⁵⁸ D. Price, *Ind. Eng. Chem.* 39, No. 9: 1143-1147 (Sept., 1947)

⁵⁹ D. Price, *Paper Trade J.* 125, No. 21: 256-261 (Nov. 26, 1947)

⁶⁰ Private communication from J. P. Bainbridge

⁶¹ W. S. Wilson and H. E. Duston, *Paper Trade J.* 117, No. 21: 223-228 (Nov. 18, 1943)

⁶² E. G. V. Percival, A. C. Cuthbertson and H. Hibbert, *J. Am. Chem. Soc.* 52, No. 8: 3448-3456 (1930)

Precipitating Rosin Size with Alum and Sulfuric Acid

Many precipitants have been tried for rosin size, aside from alum, but most of these have proved far less satisfactory than alum. Ferric sulfate has been used to a limited extent, but it requires a lower pH (about 2.5) than alum to obtain good sizing. Aluminum chloride has been proved to be a fairly satisfactory substitute for alum.⁶³

Sulfuric acid used alone is not as effective a precipitating agent as alum.⁶⁴ However, blends of sulfuric acid and alum result in better sizing and produce papers of slightly higher pH and slightly greater strength than alum alone.⁶⁵ The sulfuric acid may be added first, followed by the alum, which completes the fixing of the rosin precipitate, or the two may be added in admixture. Using bleached sulfite pulp, Price⁶⁶ found that a solution containing 3% sulfuric acid and 7% alum gave the best sizing and increased the amount of free rosin in the size precipitate. For example, the use of this mixture on rosin size containing 20% free rosin produced a precipitate of the same composition as that obtained from a 75% free rosin size, when alum was used as the only precipitant.

Precipitating Rosin Size with Sodium Aluminate

It is well recognized that a low pH in the finished paper is detrimental to the strength and permanence of the paper. This is one objection to alum as a precipitant, since the use of alum alone with rosin size makes it difficult to obtain good sizing without lowering the pH to such an extent that the strength of the paper is affected.

In order to overcome the undesirable effects of too low a pH , a small amount of alkali such as sodium hydroxide can be used in combination with alum. This permits sizing to be obtained under pH conditions where the permanence of the paper is not so greatly affected and the corrosion of the mill equipment is lessened.

Another method is to use a basic aluminum sulfate (sodium aluminate) together with alum for precipitating rosin size at the desired pH . Sodium aluminate ($NaAlO_2$) ($Na_2Al_2O_4$) is an alkaline source of alumina and differs from alum in that it contains about three times as much alumina, and this alumina is in the negative radical. An excess of sodium hydroxide is present over that necessary to neutralize all the alumina because pure sodium aluminate is unstable in solution. The best commercial products contain about 5% excess sodium hydroxide.

⁶³ C. C. Porter and W. H. Lane, *Tappi* 32, No. 10: 465-467 (Oct., 1949)

⁶⁴ T. T. Collins, Jr., H. L. Davis and B. W. Rowland, *Paper Trade J.* 113, No. 13: 154-159 (Sept. 25, 1941)

⁶⁵ D. Price and D. D. Cameron, *Paper Trade J.* 123, No. 25: 205-211 (Dec. 19, 1946)

⁶⁶ D. Price, *Paper Trade J.* 126, No. 15: 191-196 (Apr. 8, 1948)

Sodium aluminate used in conjunction with alum offers independent control of the amount of alumina added to the system and the pH of the system, with a minimum of sulfate addition. By using sodium aluminate in combination with alum, it is possible to obtain fairly satisfactory sizing over a wide range of pH . Schur and Levy⁶⁷ found that sizing begins to decrease quite rapidly at pH values higher than 4.5 when alum alone is used, but when sodium aluminate and alum are used together, good sizing can be obtained at pH values up to 6.5. Also using combinations of sodium aluminate and alum, Libby and Dohne⁶⁸ were able to obtain good sizing even with low free rosin size, at a pH between 6.0 and 8.5, depending upon the amount of white water recirculated. The results of Wilson,⁶⁹ shown in Figure X-5, show that in the presence of increasing sodium aluminate, op-

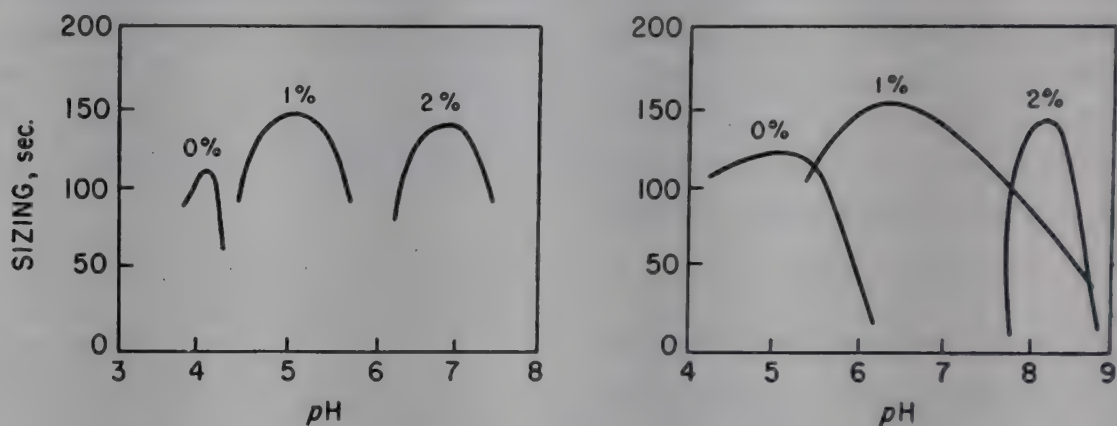


Fig. X-5. Effect of sodium aluminate (percentage on curves) on pH for optimum sizing as measured by ink resistance. At left, 1% neutral alum. At right, 1% basic alum.

timum sizing is obtained at higher and higher pH values. In every case, 1% alum was added and the amount of sodium aluminate was varied from 0 to 2%. Both neutral alum and basic alum were used.

Effect of Particle Size

It is quite generally agreed that the rosin size precipitate is attached to the fibers in the form of discrete particles and not in the form of a continuous film. The rosin particles may penetrate into the fibers, but it is likely that nearly all the size precipitate is on the outside of the fibers. Wieger⁷⁰ has stated that Bewoid size, in which the particles are about 1 micron or less in diameter, can enter the canals of pulp fibers.

The distribution of rosin size precipitate on the surface of the fibers

⁶⁷ M. O. Schur and R. M. Levy, *Paper Trade J.* 122, No. 12: 121-125 (Mar. 21, 1946)

⁶⁸ W. P. Dohne and C. E. Libby, *Paper Trade J.* 113, No. 22: 280-286 (Nov. 27, 1941)

⁶⁹ W. S. Wilson, *Paper Trade J.* 121, No. 8: 71-75 (Aug. 23, 1945)

⁷⁰ B. Wieger, *Paper Trade J.* 101, No. 5: 51-54 (Aug. 1, 1935)

has been shown by Lee⁷¹ in a series of drawings made from microscopic examination of a number of rosin-sized papers. It is shown that the rosin size particles, even when closely packed together in highly sized papers, tend to remain separate or, at the most, to form loosely combined aggregates. Sears and Kregel⁷² also found in an examination of sized fibers in an electron microscope that the precipitated rosin size exists as small discrete particles which they estimated to be about 0.25 to 1.0 micron in diameter. This evidence points to the fact that the best and most lasting sizing is obtained when the rosin size is precipitated in the form of very fine, perhaps submicroscopic, particles which are distributed uniformly and densely over the fiber surface.⁷³ This idealized condition is probably never obtained, since Sears and Kregel⁷⁴ found, even in well-sized papers, that the fibers, fibrils, and fibrillae are by no means covered with rosin particles. The sketch in Figure X-6, taken from Lee,⁷³ shows approximately how the rosin size precipitate should look in a hard-sized paper.

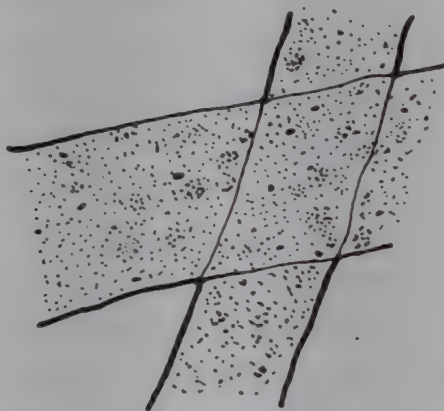


Fig. X-6. Idealized distribution of rosin size precipitate on fibers in well-sized paper.

The above observations on particle size were made by examining sized papers. Other investigators have studied the effect of particle size from the standpoint of the size of the dispersed rosin particles in free rosin size. These results have indicated that the effectiveness of free rosin size depends upon the particle size and specific surface of the dispersed rosin particles. Libby and Dennett⁷⁵ found, using suspensions of 100% free abietic acid, that particles above 350 millimicrons in radius gave poorer sizing than smaller particles. In their work, the results of which are shown in Figure X-7, the pulp was sized with 2.5% rosin size and 2.5% alum, and the

⁷¹ H. N. Lee, *Paper Trade J.* 103, No. 27: 386-390 (Dec. 31, 1936)

⁷² G. R. Sears and E. A. Kregel, *Paper Trade J.* 114, No. 12: 139-145 (Mar. 19, 1942)

⁷³ H. N. Lee, *Paper Trade J.* 107, No. 6: 53-59 (Aug. 11, 1938)

⁷⁴ G. R. Sears and E. A. Kregel, *Paper Trade J.* 114, No. 12: 139-145 (Mar. 19, 1942)

⁷⁵ F. Dennett and C. E. Libby, *Paper Trade J.* 109, No. 15: 193-199 (Oct. 12, 1939)

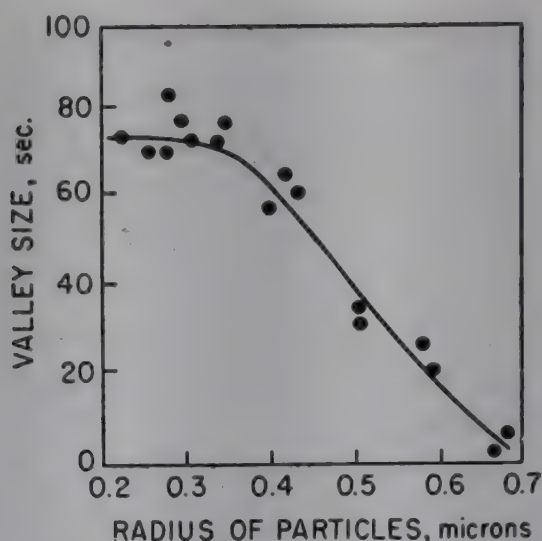


Fig. X-7. Effect of particle size in free rosin size on sizing value, using 100% free abietic acid.

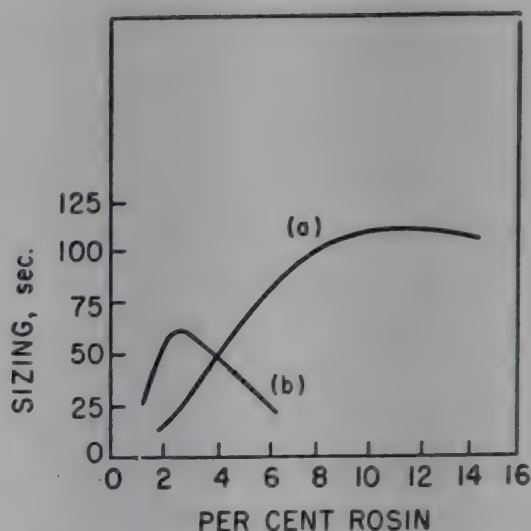


Fig. X-8. Relationship between dimensions of rosin size particles and sizing obtained for different amounts of rosin size added to paper: (a) large particles; (b) small particles.

sheets dried at 110 to 120° C. for thirty minutes to three hours. They concluded that the sizing efficiency of high free rosin size is dependent upon having the dispersed rosin particles in a finely divided state.

It is a well-known fact of colloid chemistry that small particles have a greater surface than large particles for a given weight of material. This greater surface explains why rosin size precipitated in the form of small particles is generally more effective than rosin precipitated in the form of large particles. However, it has been pointed out by Wilson and Duston⁷⁶ that this is true only when small amounts of rosin size are used. When high percentages of rosin size are used, there may be too many particles in a finely dispersed size to be effectively bonded to the fibers since, according to Wilson and Duston, only so many rosin particles can be bonded under any given condition. Assuming this is so, then, with the same number of particles attached, the larger particles would be expected to produce better sizing, since they would have more surface. These effects are illustrated in Figure X-8, where sizing was carried out with a finely dispersed size and a coarsely dispersed size, the pH being kept constant at 4.0 with alum in each case. These results indicate that fine particles are more effective than coarse particles in the range of rosin size normally used, but not so when higher percentages of rosin are used. Neitzke⁷⁷ obtained best sizing using rosin-wax mixtures when the wax particles were of relatively large size. He believed that the larger particles penetrated the fiber less, and hence remained on the surface where they were more effective.

⁷⁶ W. S. Wilson and H. E. Duston, *Paper Trade J.* 117, No. 21: 223-228 (Nov. 18, 1943)

⁷⁷ O. F. Neitzke, *Paper Trade J.* 100, No. 17: 219-222 (Apr. 25, 1935)

Comparison of Pulps for Ease of Sizing

As every papermaker knows, there is a great difference between different pulps in respect to their ease of sizing. This is shown by the data of Robinson,⁷⁸ reported in Table III, comparing different pulps for their ease

TABLE III

RELATIVE SIZABILITY OF DIFFERENT PULPS
2% rosin size added, alum added to a pH of 4.5

Per cent retention of size	Type of pulp	Freeness	Valley size, sec.	Dry indicator, sec.
69	Groundwood	260	42	32
59	Unbleached kraft	370	21	67
54	Unbleached Mitscherlich	390	14	44
47	Unbleached sulfite	385	13	62
66	Semi-bleached kraft	370	21	75
49	Bleached sulfite	360	15	46
52	Alpha	390	18	43
68	Rag	370	4	15

of sizing. All these pulps were sized under the same conditions, using 2% rosin size and the pH adjusted to 4.5 with alum, but as can be seen, the unbleached pulps were generally easier to size than the bleached pulps. One interesting point about these data is that there is no relationship between the per cent retention of size in the paper and the sizing value. Also, there is no correlation between the results obtained on the different sizing tests. The results of Wilson,⁷⁹ illustrated in Figure X-9, show that ground-

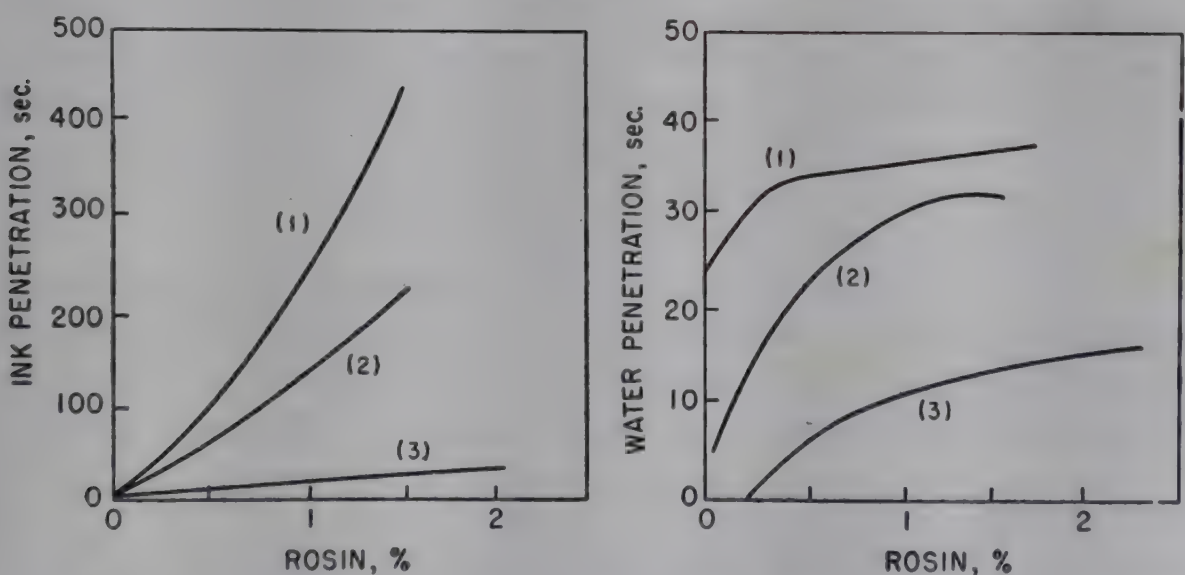


Fig. X-9. Relative sizability of different pulps as measured by the ink and water resistance tests: (1) groundwood; (2) sulfite; (3) rag.

⁷⁸ S. J. Robinson, *Paper Trade J.* 103, No. 7: 130-138 (Aug. 13, 1936)

⁷⁹ W. S. Wilson, *Paper Trade J.* 123, No. 24: 198-202 (Dec. 12, 1946)

wood is easier to size than sulfite and that both are easier to size than rag. In these experiments, the rosin was added in alcoholic solution and 5% alum was added.

The explanation of why different pulps vary in their ease of sizing is not entirely clear. Part of the explanation can be found in the behavior of sodium resinate solutions in the presence of different pulp fibers. When concentrated solutions of sodium resinate are diluted, some hydrolysis of sodium resinate into sodium hydroxide and colloiddally dispersed rosin takes place. The extent of hydrolysis of sodium resinate at the concentrations existing in the beater (0.001–0.005 *N* in sodium resinate) has been a matter of conflicting reports,^{80,81} but Bialkowsky⁸² has shown that hydrolysis occurs to the extent of only a few per cent in pure water at these concentrations. However, he found that pulp fibers force the hydrolysis of sodium resinate so that up to 60% of the resinate is converted into free rosin in the presence of certain fibers. This forced hydrolysis of sodium resinate by pulp fibers can be explained on the basis that pulp fibers preferentially adsorb sodium ions and sodium hydroxide⁸³ which are present in small amounts due to the natural hydrolysis of the rosin soap. This causes further hydrolysis to take place, thereby increasing the amount of free rosin and reducing the amount of aluminum diresinate in the precipitate. Robinson⁸⁴ showed that exposure of rosin size to pulp fibers for a period of twenty-four hours before precipitation tends to increase the free rosin content of the precipitate. Presumably, this free rosin liberated by the fibers has a much smaller particle size than the free rosin contained in free rosin size, and consequently does a more effective job of sizing.

Wilson⁸⁵ believes that the ion exchange properties of the pulp determine the number of "bonds" available for fixing rosin size precipitate on the fibers and that the greater exchange properties of impure pulps explain why these pulps are easier to size than pure pulps. The ion exchange capacity of pulp can be measured by converting the pulp to the hydrogen form and then titrating with sodium hydroxide.

As shown by the data in Table III, unbleached pulps are generally easier to size than bleached pulps. As a rule, sulfate pulps are easier to size than sulfite pulps. High alpha pulps are very difficult to size. Ecke⁸⁶ found that the ease of sizing is closely related to the pentosan content of

⁸⁰ A. Haug, *Paper Trade J.* 76, No. 26: 45–48; 77, No. 2: 51–54 (June 28, July 12, 1923)

⁸¹ F. C. Beedle and T. R. Bolam, *J. Soc. Chem. Ind.* 40, No. 4: 27 (1921)

⁸² H. W. Bialkowsky, *Paper Trade J.* 97, No. 13: 141–158 (Sept. 28, 1933)

⁸³ M. L. Downs, *Paper Trade J.* 107, No. 16: 30–35 (Oct. 20, 1938)

⁸⁴ S. J. Robinson, *Paper Trade J.* 103, No. 7: 130–138 (Aug. 13, 1936)

⁸⁵ W. S. Wilson, *Paper Trade J.* 119, No. 1: 3–4 (July 6, 1944)

⁸⁶ A. Ecke, *Papier-Fabr.* 31, No. 50: 667–673 (Dec. 10, 1933)

the pulp, and Goldsmid⁸⁷ reports that pulps with less than 4.5% of hemi-cellulose are very difficult to size. Sutermeister⁸⁸ reports that a preliminary treatment with bleach improves the ease of sizing of alpha pulps.

Pulps which have been improperly washed after cooking and bleaching are very difficult to size. The same situation exists in the case of rag stock or deinked waste papers when wetting agents are used in the cooking or de-inking process. If these agents are not thoroughly removed from the pulp, they will interfere with the sizing.

Stock Conditions Affecting Sizing

Paper mills frequently experience, to some degree, variations in the internal sizing of paper. In some cases the trouble is not serious, but in other cases, the results undergo considerable variation in spite of the fact that no known changes have been made in the operating process. In severe cases, sizing qualities may be completely lost, resulting in the production of considerable unsalable paper. These situations are obviously serious and require prompt action.

In times when sizing values are low, the first thought is to increase the amount of rosin size employed. This often helps the situation, but cannot be carried too far, inasmuch as the sizing value usually reaches a maximum at approximately 2.0 to 4.0% rosin size on the basis of the fiber, and thereafter further increments of size do very little good. In this and the following sections, some of the more important variables affecting sizing results are discussed.

The results obtained in sizing depend upon the condition of the rosin size precipitate in the finished paper. Two papers having the same fiber furnish and containing the same amount of rosin size precipitate may have widely different sizing values, depending upon the condition and distribution of the precipitated rosin size in the sheet. Nearly all the components in the furnish affect the sizing value. Furthermore, the physical conditions to which the stock is subjected, such as the amount of beating, the temperature of the stock, the order in which alum, size, and filler are added, the handling of the stock on the wire, and the conditions of pressing and drying, all influence the sizing results. Hence, in order to understand sizing, it is necessary to understand the reactions which take place at each important step in the papermaking process.

The degree of beating or physical treatment of the fibers is an important factor in sizing. As a general rule, the more the stock is beaten, the higher the sizing value obtained with a given amount of rosin size, although

⁸⁷ P. Goldsmid, *Papeterie* 68, No. 9: 261-266; No. 10: 293-296; No. 11: 330-333; No. 12: 362-366 (Sept.-Dec., 1946); 69, No. 1: 2-73 (Jan., Mar., 1947)

⁸⁸ E. Sutermeister, *Paper Ind.* 29, No. 11: 1600-1603 (Feb., 1948)

this is not strictly true in all cases. The improvement in sizing due to beating is probably the result of decreased porosity of the paper rather than any effect which beating has on the condition of the rosin size precipitate. As an exception, it should be noted that the Valley size test usually decreases as the sheet becomes denser. For best results, rosin size should be precipitated after the refining of the stock has been completed, although this procedure is not generally followed in commercial practice.

The length of time during which the size is in contact with the pulp is a factor in sizing. According to Harrison,⁸⁹ the longer the period of contact between the rosin size and the fibers, the better the sizing, up to a period of about twenty to forty minutes. He also found that for best results, the sheet should not be formed for an appreciable period (15–20 minutes) after the alum has been added. However, too long an interval between the time the size is precipitated and the sheet is formed may be harmful to the sizing result, as evidenced by the loss in sizing which sometimes results when sized stock is left over the weekend. If this occurs, addition of fresh alum may restore the sizing. The results obtained depend upon the type of size used and the conditions under which the sizing is carried out.

Good distribution of rosin size in the beaters is essential before the alum is added. In this respect, the consistency of the stock is of importance, since poor distribution of rosin size may result if the consistency is too high. Best results are obtained when the sizing reaction is carried out at a stock consistency of 4 to 6%.

If the rosin size is not allowed sufficient time to disperse in the beater, an early addition of alum will result in slack sizing. This condition can be corrected by (1) using lower consistencies in beater furnishes, (2) using dilute solutions of rosin size and alum, (3) using shower pipes for the addition of rosin size and alum, (4) allowing sufficient time between rosin size and alum additions, and (5) making rosin size and alum additions very slowly. It has been reported⁹⁰ that the retention of the rosin size precipitate in the paper decreases with a decrease in the consistency at which the paper is formed, particularly below a consistency of 0.5%.

Effect of pH on Sizing

Through the years, paper chemists have developed the conviction that the best and most efficient sizing is obtained at a pH between 4.7 and 5.5 at the wire or headbox of the paper machine. This, however, varies according to mill conditions and the type of pulp, as shown by Olsen and

⁸⁹ H. A. Harrison, *Paper-Maker* (Apr. May, June, 1932)

⁹⁰ V. R. Croswell, A. C. Dreshfield and H. F. Heller, *Paper-Maker* 2, No. 1: (Jan., Feb., 1933)

Gortner,^{91,92} who obtained optimum results at a pH between 4.5 to 6.5 for commercial pulps, and between 4.0 to 4.5 for purified pulps. In commercial practice, a somewhat higher pH is generally maintained in the case of unbleached sulfate than in the case of bleached pulps. It should be pointed out that limitations in operating conditions or special requirements in the final paper do not always permit operating at the pH value for optimum sizing.

Many mills make it a practice to check the pH in the beater, headbox, and tray water, and in some cases, to check the total acidity of the system at these points. A complete survey should include a check on the furnish water and a test at the beater after each addition of water, pulp, reclaimed stock, starch, rosin size, and alum. The effect of the mill water on sizing is discussed in the following section.

Many chemists have questioned the value of pH measurement as an aid in studying sizing, on the basis that a measurement of the pH during sizing furnishes a measurement of only one variable, and that this variable is of considerably less importance than some of the other variables, such as the quantity of alumina, the concentration of aluminum ions, or the amount of sulfate ion present. However, pH and total acidity control are still the most effective tests for controlling sizing in the mill, and there are many practical advantages to be obtained from the control of these variables. Many mills have set up automatic pH control devices to aid in maintaining uniform sizing without the difficulties encountered in manual operation. Control systems are usually set up at the paper machine where control of the pH is obtained by the automatic feed of alum solution just prior to sheet formation. In some systems, alum is added in the normal manner at the beaters and control is accomplished at the machine by the automatic addition of an alkaline material such as sodium aluminate.

Automatic control of the pH value between 5.0 to 5.5 has proved to be the most effective range in most cases. Under ordinary circumstances, the sizing tends to decrease when the operation is carried out at pH values above 5.5, and no advantage is realized in operating much below pH 5.0. Mention should also be made of other advantages which occur from the use of automatic pH control. Some of these are: less fluctuation in filler retention due to pH variation; less variation in color due to pH changes; reduced alum consumption; reduced foaming difficulties; more efficient operation of white water save-all systems due to uniform pH value of water (this is very important where solids of white water are recovered by chemical treatment); reduced corrosion of mill equipment; improved physical

⁹¹ S. R. Olsen, *Tech. Assoc. Papers* 12, No. 1: 112-115 (May, 1929)

⁹² S. R. Olsen and R. A. Gortner, *Tech. Assoc. Papers* 12, No. 1: 117-120 (May, 1929)

strength qualities and aging characteristics of the paper. Furthermore, the government and other users of paper often have specifications for pH value, and mills without automatic pH control equipment often have difficulty meeting these specifications.

Effect of Water on Sizing

The water used in making up the furnish has an important effect on the sizing result. Hard water is particularly objectionable, and in many cases, has been the direct cause of poor sizing. Thus, if the mill water is excessively hard, it should be softened.

If softening of the mill water is not feasible, the water can be treated with a small amount of sulfuric acid or alum prior to the addition of the size and then additional alum added later to set the size. Adjustment of hard water to a pH of 5.0 in this way before the size is added improves the sizing and reduces the amount of alum required to set the size.⁹³ In general, acid is better than alum for adjusting the pH of the water, since excess aluminum ions or excess alumina in the system before the size is added tend to decrease the sizing, although Brauns⁹⁴ found that 0.2 to 0.4% alum on the pulp added before the size improved the sizing, regardless of the water used and the pH. The addition of too much acid to the stock before the rosin size is added results in no sizing at all.

The effect of hard water on sizing depends somewhat upon the pH of the system. Work by Price⁹⁵ on waters containing calcium bicarbonate showed that the amount of calcium in the size precipitate increases as the pH of the water is increased. At pH values below 6, the size precipitate was found to contain free rosin acids; at pH value between 6.0 and 6.5, it was found to contain a material corresponding to one resin acid and one calcium diresinate; at pH values of 7.0 or above, it was found to contain a material corresponding to calcium diresinate. This is one explanation of why calcium salts are detrimental to sizing in alkaline waters and harmless or beneficial in acid waters.⁹⁶

In mills where the system is well closed, the furnish water for the beaters may build up with alum (and sodium sulfate). Although this increasing acidity causes no trouble in some mills, the safest and most satisfactory procedure is to neutralize the stock previous to rosin size addition. Alkalies such as silicate of soda and lime are satisfactory for this purpose. The circulation of too much white water is also harmful because of the excess

⁹³ D. Price and D. D. Cameron, *Paper Trade J.* 123, No. 25: 205-211 (Dec. 19, 1946)

⁹⁴ O. Brauns, *Svensk Papperstidn.* 52, No. 23: 579-586 (Dec. 15, 1949)

⁹⁵ D. Price, *Paper Trade J.* 126, No. 15: 191-196 (Apr. 8, 1948)

⁹⁶ D. Price and D. D. Cameron, *Pulp Paper Mag. Canada* 47, No. 3: 142-148. Convention Issue (1946)

sulfate ion which is built up in the system. In a situation where the recirculated white water for furnishing is suspected of being harmful to sizing, trials with fresh water may prove the point. White water which has been clarified can be used in the sprays on the paper machine with better results on the sizing than obtained from the use of fresh water sprays.

At certain times of the year, raw waters and certain recovered waters from the pulp mill contain colloidal organic material of an acid nature. This may become attached to the pulp fibers during washing and subsequently interfere with the proper fixing of rosin size precipitate on the fibers.⁹⁷ The remedy is to treat the water with alkali or, in extreme cases, to resort to filtration. Seasonal changes sometimes result in chemical changes in the water supply which affect the sizing operation.

Effect of Temperature on Sizing

It is a well-known fact that good results with rosin size are more difficult to achieve in warm weather than in cold. Mills making highly sized papers often experience a great deal of difficulty in meeting their sizing requirements during the summer months, due to the higher temperature of the raw water. Rag mills, in particular, experience trouble in this respect because of the increased temperature brought about by the long beating cycles. Even short beating cycles in certain stock preparation equipment, mechanically designed so that considerable heat is developed during beating, is sufficient to raise the temperature to the point where the sizing is affected. Many mills are finding it necessary to close up their systems and reuse increasing amounts of their white water in an effort to improve stream pollution problems, and this recirculated water tends to increase the temperature, thereby contributing to sizing difficulties.

Price⁹⁸ studied the effect of temperature on sizing in a range from 16 to 50° C. and found that the lowest temperature gives the best sizing. This agrees with practical experience, as a result of which it is pretty generally agreed that temperatures should be maintained below about 35° C. Brecht and Liebert⁹⁹ found 40° C. to be optimum for sizing, but this is unusual and must have been due to special conditions. The results depend somewhat upon the type of pulp, it having been reported that high temperature has a more harmful effect on the sizing of bleached sulfite than on either unbleached sulfite or unbleached sulfate.¹⁰⁰ At temperatures of 70 to 75° C., it is practically impossible to obtain any sizing at all on any pulp.

In cases where trouble is experienced with poor sizing in the summer

⁹⁷ C. C. Irving, *Paper Mill* 62, No. 45: 18, 20-21 (Nov. 11, 1939)

⁹⁸ D. Price, *Paper Trade J.* 127, No. 8: 43-45 (Aug. 19, 1948)

⁹⁹ W. Brecht and E. Liebert, *Papier-Fabr.* 41: 9-16, 18-27 (1947)

¹⁰⁰ J. A. Hester, F. Bridge and H. A. Harrison, *World's Paper Trade Rev.* 128, No. 8: 487-534 (1947)

months, the coolest possible water should be used and the best sizing practice observed. One expedient is to add the size late in the beating cycle to avoid long exposure to high temperatures. It is the rosin size precipitate which is most affected by heat and it is therefore advisable to add the alum to the furnish as late as practical.

Price¹⁰¹ found that the destructive effect of high temperature is a function of the time during which the size precipitate is exposed to the high temperature, as well as the actual temperature. The greatest loss in sizing was found to take place during the first few hours. High temperature apparently has little effect on the electrostatic charge on the size precipitate, but probably affects the degree of coagulation or the hydration of the precipitate.¹⁰²

High temperatures tend to aggravate trouble with sticking on the presses of the paper machine. This trouble arises from pitch in the pulp which is softened at high temperature so that it is more likely to agglomerate into large particles. Similar trouble can be caused by rosin size.

Effect of Protective Colloids on Sizing

The use of protective colloids in the preparation of high free rosin size by the Bewoid and Prosize processes has already been discussed. Protective colloids can also be added directly to the beater before the size is pre-

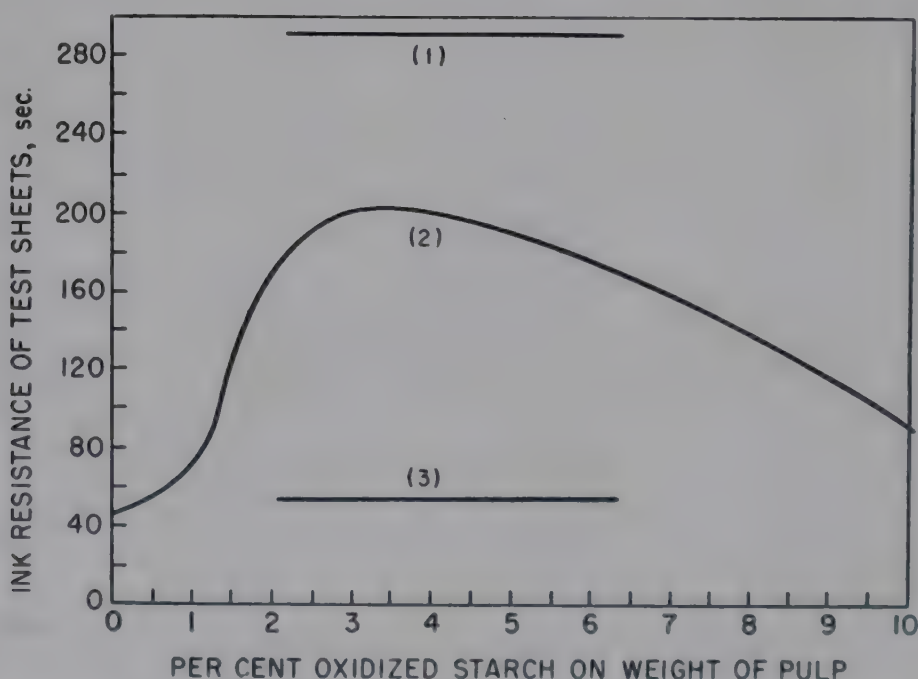


Fig. X-10. Effect of oxidized starch on the sizing obtained with neutral rosin size: (1) 3.6% rosin size, no starch; (2) 1.8% rosin size containing various amounts of oxidized starch; (3) 1.8% rosin size, no starch.

¹⁰¹ D. Price, *Paper Trade J.* 127, No. 8: 43-45 (Aug. 19, 1948)

¹⁰² H. A. Harrison, *Proc. Tech. Sec., Papermakers' Assoc. Gt. Britain Ireland* 12: 61-208 (Apr., May, June, 1932)

cipitated. When used in this way, protective colloids cause the rosin size to be precipitated in a more effective form. Their use can be considered when sizing results are poor.

Oxidized starches are sometimes used in the above manner, and the results obtained are usually worth while. It is possible to increase the ink resistance (measured by the ink flotation method) on sulfite bond from 25 to 50% by using 3 to 5% oxidized starch on the weight of the pulp. The starch is much more effective if it is thoroughly cooked before adding to the beater, and if it is added between the rosin size and the alum. The effect of adding increased amounts of oxidized starch to a furnish of bleached sulfite containing 1.8% of neutral rosin size in a laboratory beater is shown in Figure X-10. As can be seen from these results, the starch must be added in high percentages, i.e., from 2½ to 5% on the weight of the pulp in order for it to be fully effective. Beyond about 4 to 5% oxidized starch on the weight of the pulp, there is a definite decrease in the sizing value. This reduced sizing at higher starch additions is apparently due to the starch acting in competition with the rosin size for the available alum in the system, since increasing the amount of alum added results in an increase in the amount of starch which can be advantageously used.¹⁰³ Other effects of adding starch at the beater are discussed in Chapter VII.

Animal glue and technical gelatin are sometimes added to papermaking stock to improve the sizing (see Chapter VIII). Sodium silicate may be added, usually to increase the stiffness and rattle of the paper, but also in some cases to improve the retention of rosin. It has been stated that it is possible to precipitate a silicate-rosin complex in the beater by lowering the pH of the beater to at least 4.6 with alum.¹⁰⁴

Effect of Fillers on Sizing

In general, fillers have an adverse effect on sizing. A few fillers such as gypsum and talc have been reported as improving the sizing,¹⁰⁵ but this is unusual. Titanium appears to help the sizing in certain cases. Because of their harmful effect, it is generally best to add fillers after the rosin size and alum have been added.

Calcium carbonate is particularly harmful to sizing, and it is difficult to size papers containing a high percentage of this filler. When sizing difficulties arise, it is well to check fillers being used, even though they are thought to be carbonate-free. If the furnish contains reclaimed papers of unknown history, it is possible that calcium carbonate may be present as

¹⁰³ Unpublished work by A. Aronoff, New York State College of Forestry, Syracuse, N. Y. (June, 1950)

¹⁰⁴ "Silicate P's and Q's," *Philadelphia Quartz Company Bulletin*, Vol. 25, No. 7 (July, 1945)

¹⁰⁵ P. Goldsmid, *Papeterie* 68, No. 9: 261-266; No. 10: 293-296; No. 11: 330-333; No. 12: 362-366 (Sept.-Dec., 1946); 69, No. 1: 2-73 (Jan., Mar., 1947)

filler or coating. Since all normal fillers reduce sizing, it is well to check the filler content of the paper at times when sizing values are low.

Effect of Sheet Formation on Sizing

Sheet formation is a very significant factor in sizing, particularly in the case of light-weight papers. Nearly all the variables in machine operation affect the formation of the finished paper and thereby affect the sizing. In this connection, it should be pointed out that some defoaming agents which contribute to improved sheet formation will sometimes improve the sizing, whereas other defoaming agents tend to reduce sizing if used in excess.

Sizing tests made on handsheets prepared from stock taken at various points at the wet end of the machine will indicate if sizing difficulties are due to machine conditions or to conditions originating back in the stock preparation. Such effects as dilutions and action of jordans can be determined in this way.

Retention of fiber and filler fines in sheet formation has a considerable effect on the sizing results. Slow stock is very effective in retaining these fines, and further increases in retention can be obtained by adding materials such as Sveen glue or activated silica. The recovered stock from white water clarification systems contains considerable fines, and when this material is returned to the paper machine and incorporated with the original stock, sheet qualities change considerably and definite improvements in sizing characteristics are usually noted.

Continuous addition of sizing agents at various points at the wet end of the paper machine has been found effective in some mills. In these operations, dilute solutions of rosin size, alum, and alkali such as sodium aluminate are metered to the stock at such points as the jordans, mixing boxes, screen inlets, and headbox.

Under certain circumstances, paper exhibits a condition known as two-sidedness, in which the sizing, as measured by the writing qualities, is not the same on the two sides of the sheet. When this condition occurs, the writing qualities are usually better on the top or felt side of the paper than they are on the wire side. The principal cause of two-sidedness is high machine speed, which causes the rosin size precipitate to be washed or sucked out of the underside of the paper on the wire or at the suction boxes. Differences in the wet pressing on the two sides of the paper will also, under certain circumstances, result in a two-sided sizing effect. Uneven pressing across the width of the paper should be avoided, inasmuch as it results in uneven sizing across the sheet.

Effect of Drying on Sizing

The temperature at which the paper is dried has long been recognized

as an important factor in sizing. Heat is necessary to obtain the maximum sizing effect, but the method of applying the heat is also important. This can be illustrated in the laboratory by drying a sample of paper in an oven and another sample of the same paper on a steam-heated drier roll. It will be found that the sample dried in contact with the heated roll will have an appreciably higher sizing value than the sample dried in the oven.

Some chemists believe that the heat in drying produces a sintering of the rosin size precipitate in the paper, thereby increasing the adhesion of the precipitate for the fiber. One advantage claimed for free rosin size is the lower sintering temperature of free rosin compared with that of aluminum resinate. The optimum temperature for the initial drying of sized papers is generally considered to be between 175 to 212° F. For best results, the heat should be applied while the paper is in a moist condition. Exposure of poorly sized paper to steam will sometimes improve the sizing value.

The rate of water removal during drying is an important factor in sizing. If the temperature is raised too rapidly, the vapor pressure within the paper will exceed the rate of moisture escape, with the result that the rosin size precipitate attached to the fiber will be disrupted. If heavy papers are heated too rapidly, a temporary film may be formed on the surface of the paper which is later disrupted by vapor escaping from the interior. Under severe conditions, the rosin size precipitate may migrate to one surface of the sheet.

For best results, it is desirable to graduate the temperature of drying. Many mills use moderate temperatures in the first and last drier sections and build up to maximum steam pressure in the middle section. Other mills prefer to build up gradually to the optimum temperature (approximately 210° F.) at the dry end. In any event, the optimum temperature should not be reached until the sheet contains less than 40 to 50% moisture, which means that excessive temperatures in the initial driers should be avoided. Individual surface drier temperatures are easily determined, and when the data are plotted, the charts show clearly any abnormal situations. In this way, difficulties in the drier sections due to poor condensate removal, inefficient traps, etc., can be detected.

Effect of Calendering on Sizing

Very little is actually known about the effect of calendering on sizing, but it is commonly recognized that calendering is harmful to sizing. On machine-finished papers, the loss in sizing may vary from a slight loss for low finish papers to an appreciable loss in the case of heavily calendered papers. Calendering can be particularly harmful to sizing in the case of light-weight papers which are given a high finish on the paper machine.

On the other hand, supercalendered sheets which are pretreated in a steam conditioning box ahead of the calendering operation often show an improvement in sizing.

The proper temperature for calendering to obtain the best sizing is a debatable point. It has been reported that a low temperature should be used on the wet stack and a high temperature on the dry stack. The moisture content of the paper at the time of calendering is another important variable, and in general, calendering is far more destructive when the moisture content is high (7–8%) than when the sheet is comparatively dry (4–5%). The amount of pressure used in calendering is also important, since excessive pressure reduces or even destroys the sizing. In the case of paperboards which are given a water finish, there may be a leaching of size from the sheet by the action of the hot water in the water boxes.

Internal Sizing with Other Substances

In addition to rosin, several other sizing agents have been proposed for internal sizing, either as a partial or complete substitute for rosin. Wax emulsions have come into rather extensive use, and some of the new synthetic products are also being used. A few of these new materials are discussed in the following sections.

Sizing with Wax Emulsions and Rosin-Wax Emulsions

Paraffin is a relatively inexpensive product with a high degree of water repellency, and it is logical that it would be tried for internal sizing. The paraffin wax emulsions offered to the paper industry in the early days were unsatisfactory because of their relatively large particle size,¹⁰⁶ but since that time, highly satisfactory wax emulsions have been developed for use in sizing paper.

Both alum precipitable and non-alum precipitable wax emulsions are used in beater sizing.¹⁰⁷ Alum is necessary to “set” both types, but in the precipitable grades, alum or acid must be used for its additional effect in breaking the emulsion. In setting the size with alum, a low pH may be required in some cases,¹⁰⁸ but Neitzke¹⁰⁹ found that the optimum pH for the setting of one all-wax size was about 6.4 to 6.6.

In beater sizing with wax emulsions, it is desirable to use an emulsion which has been diluted to 5 to 10% wax solids. The emulsion is added to the stock near the end of the beating period, but beating should be continued for 5 to 20 minutes in order to insure uniform distribution of the wax.

¹⁰⁶ R. M. Cobb, D. S. Chamberlin and B. A. Dombrow, *Paper Trade J.* 97, No. 10: 111–114 (Sept. 7, 1933)

¹⁰⁷ J. C. Dean, *Paper Mill News*, Superintendents' Number, 74–78 (June 16, 1945)

¹⁰⁸ L. K. Arnold and J. B. McLeod, *Paper Ind.* 25, No. 2: 156 (May, 1943)

¹⁰⁹ O. F. Neitzke, *Paper Trade J.* 95, No. 18: 201–203 (Nov. 3, 1932)

Alum is always required to set the wax, but somewhat different procedures are recommended for soap type emulsions and acid-stable emulsions, and these are listed below:

Soap type emulsion

Add rosin size and mix.
Add diluted wax emulsion and beat 10
to 20 minutes (pH 7.0 or higher).
Add alum.

Acid-stable emulsion

Add rosin size and mix.
Add alum and mix.
Add diluted emulsion and beat 10 to 20
minutes. (The emulsion can also be
added before the alum with good re-
sults.)

An alternative method which can be used with acid-stable emulsions is to mix the emulsion and alum together and add the mixture to the beater.

Wax emulsions work particularly well for the sizing of asbestos papers, carbonate-filled papers, hanging papers, tag, envelope, and milk bottle stock, but other grades, even high-grade writing papers, may be sized with a small amount of wax in combination with rosin size. Wax emulsions have an advantage over rosin size in that once the wax particles have been precipitated, the paper can be brought back to a higher pH, even to a pH of 10, without destroying the sizing. For this reason, Rafton¹¹⁰ recommends wax emulsions for sizing alkaline-filled papers where ordinary rosin size cannot be used. He suggests¹¹¹ that the alum be used to precipitate the emulsion before the carbonate is added. There are several patents pertaining to the use of wax emulsions in alkaline-filled papers.¹¹²⁻¹¹⁴ Other advantages of wax emulsions are reduced foam in the mill system and improved paper properties such as reduced curl, greater pliability, improved finish, better printing qualities, higher water resistance, and improved aging of the sized paper. Wax sizes are superior to rosin size in hot pulp systems, and therefore find application in some board mills where high stock temperatures are employed.

The addition of a small amount of rosin size to an all-wax size generally increases the efficiency and, generally speaking, the use of wax emulsions is limited to the replacement of 20-40% of the rosin size normally used.^{115, 116} Mixtures of rosin and wax which contain wax and free rosin emulsified in rosin soap have sometimes been used. One process¹¹⁷ for preparing rosin-wax size calls for subjecting melted rosin, unsaponifiable wax, and hot alkali to the action of a specially designed dispersion machine in which saponifica-

¹¹⁰ H. R. Rafton, U. S. 2,020,328 (Nov. 12, 1935)

¹¹¹ H. R. Rafton, U. S. 1,848,659 (Mar. 8, 1932)

¹¹² O. Kress and G. Johnson, U. S. 2,059,465 (Nov. 3, 1936)

¹¹³ E. Sutermeister and J. A. Warren, U. S. 1,838,969 (Dec. 29, 1931)

¹¹⁴ H. R. Rafton, U. S. 1,819,441 (Aug. 18, 1931)

¹¹⁵ O. F. Neitzke, *Paper Trade J.* 95, No. 18: 201-203 (Nov. 3, 1932)

¹¹⁶ J. C. Dean, *Paper Mill News*, Superintendents' Number, 74-78 (June 16, 1945)

¹¹⁷ O. F. Neitzke, *Paper Trade J.* 100, No. 17: 219-222 (Apr. 25, 1935)

tion of the rosin is followed almost instantly by the dispersion and stabilization of the wax. The rosin soap formed in this process stabilizes the wax and the free rosin in the form of particles which are claimed to have an average diameter of $1/20,000$ in. There is relatively little rosin-wax size sold as such, although one manufacturer sells a plasticized rosin size containing about 20% wax.

Certain advantages are to be gained from the use of rosin-wax combinations compared with straight rosin size. Neitzke¹¹⁸ reports that 65 lb. of rosin-wax size (which contained 80% rosin and 20% wax) gave the same sizing as 100 lb. of straight rosin size. However, Griesinger and Reynolds¹¹⁹ found that the results depend entirely upon the grade of pulp being sized, groundwood being particularly adaptable to sizing with wax. Their results indicate that the amount of wax in a rosin-wax size should not exceed definite proportions in certain pulp furnishes, and Neitzke¹¹⁸ also found this to be true, although not in the same proportion, nor with the same pulps. The results are apparently affected by variables not entirely understood, and results obtained under certain conditions do not appear to apply under other apparently similar conditions. The results of Neitzke in Figure X-11

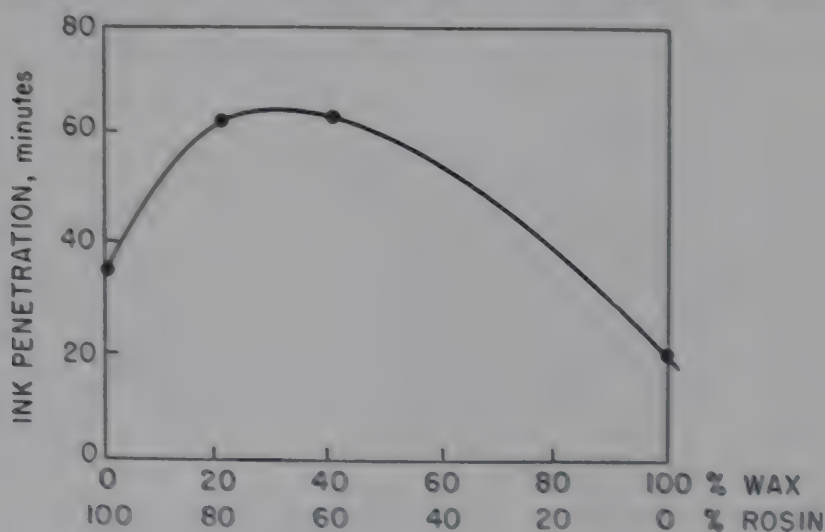


Fig. X-11. Effect of amount of wax in a rosin-wax size on the sizing obtained on bleached sulfite.

show that the sizing efficiency of a rosin-wax mixture in a bleached sulfite furnish increases up to a wax content of about 25%, and thereafter decreases with increasing wax content.

A further advantage of rosin-wax size not already mentioned is that the sizing obtained with rosin-wax sizes continues to improve up to nearly 5% total size on the weight of the pulp, whereas the sizing obtained with straight rosin size tends to decrease greatly in efficiency above 2 to 4% size.

¹¹⁸ O. F. Neitzke, *Paper Trade J.* 95, No. 18: 201-203 (Nov. 3, 1932)

¹¹⁹ W. K. Griesinger and M. H. Reynolds, *Paper Ind.* 22, No. 3: 248-251 (June, 1940)

These effects are shown in Figure X-12.¹²⁰ In some cases, even higher

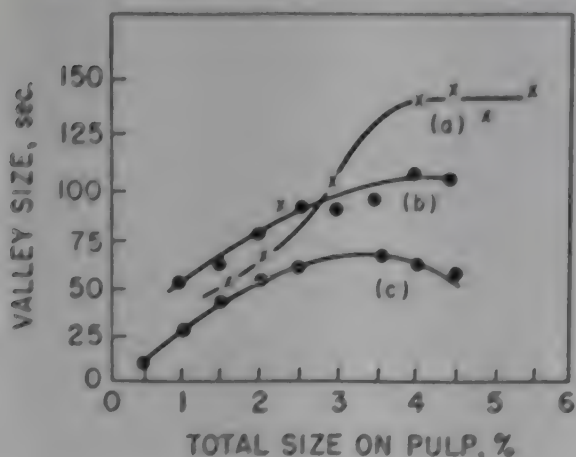


Fig. X-12. Effect of amount of wax in total size added to pulp on the sizing value: (a) 1.0% rosin plus wax; (b) 0.5% rosin plus wax; (c) rosin.

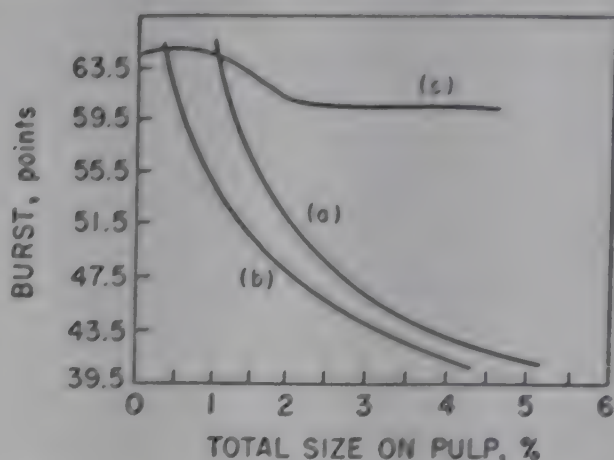


Fig. X-13. Effect of amount of wax in total size added to the pulp on bursting strength: (a) 1.0% rosin plus wax; (b) 0.5% rosin plus wax; (c) rosin.

percentages of rosin-wax size can be used to advantage, as for example, when increased pliability, softness, and finish of the paper are desired. One of the drawbacks to the use of rosin-wax size is the greater loss in strength (burst and tensile) compared to that obtained with straight rosin size. This is shown in Figure X-13. Referring to the results shown in this figure and taking paper sized with 2% size as a standard, it can be seen that a 50-50 mixture of rosin and wax produces a paper with a bursting strength about 15% lower than that obtained with straight rosin size.

Heating of the sized paper is necessary for the development of satisfactory sizing from wax emulsions, just as it is with rosin-sized papers. However, it has been postulated that less heat is required with rosin-wax size than with straight rosin size because of the lower fluxing temperature of the wax.¹²¹ Neitzke postulates that wax, which is more easily fluxed and is less viscous than rosin, tends to penetrate into the capillaries of the fibers to a greater extent than rosin, thereby producing less of a surface deposit on the fibers.

Sizing with Other Waxes

Montan wax has received some attention as an internal sizing agent in European mills, although it has never been used to any extent in the United States. Montan wax is a complex mixture of hydrocarbons, organic acids, and esters, and has a somewhat lower melting point than rosin. The wax can be used by itself or in mixture with rosin or other waxes for

¹²⁰ W. K. Griesinger and M. H. Reynolds, *Paper Ind.* 22, No. 3: 248-251 (June, 1940)

¹²¹ R. M. Cobb, D. S. Chamberlin and B. A. Dombrow, *Paper Trade J.* 97, No. 10: 111-114 (Sept. 7, 1933)

internal sizing. It has been claimed¹²² that Montan wax produces a paper of higher strength, greater softness, better finish, and higher water resistance than that obtained with rosin-sized papers. One advantage of Montan wax is that best results are obtained at a pH between 7.0 to 7.5, which makes it possible to obtain sizing in the presence of alkaline fillers.¹²³

Many other wax and wax-like materials can be used for sizing. In fact, almost any type of waxy material can be used in emulsified form for the sizing of paper. Lane¹²⁴ suggests the use of fatty acids containing nine or more carbon atoms. Hans and Raney¹²⁵ describe a composition prepared by stirring finely divided cumar resin (melting point, 110–115° C.) into water containing sodium silicate and oleic acid in the following proportions:

Cumar resin	300 parts
Water	290 parts
Oleic acid	10 parts
Sodium silicate	14 parts

During World War II, when rosin was difficult to obtain, aromatic petroleum extracts in emulsified form were suggested in England as a partial replacement for rosin size.¹²⁶

Synthetic resin emulsions have been suggested for beater sizing, particularly the alkyd resin emulsions which can be made in grades that are precipitable by acids or alum.¹²⁷ However, resin emulsions are usually added for their effect on the physical properties of the paper, rather than for their sizing effect. The use of resins for beater addition is discussed in Chapter XXI.

Sizing with Mersize

One of the important new sizing agents is a rosin-maleic anhydride condensation product sold under the trade name of Mersize. This material differs from rosin size in that each molecule contains three carboxylic acid groups compared to a single group for rosin. It has the physical form of a solid resinous material, but it is usually sold as a viscous, clear, amber-colored alkaline water dispersion containing 51% resin.¹²⁸

Mersize is readily dispersible in cold water up to concentrations of 3%, but dispersions more concentrated than this are likely to form gels upon standing and should not be used. Mersize should not be dispersed in

¹²² Wochbl. *Papierfabr.* (Sept. 2, 1933)

¹²³ B. von Possanner, *Papier-Fabr.* 33, No. 31: 257–260 (Aug. 4, 1935)

¹²⁴ G. T. Lane, U. S. 1,840,399 (June 12, 1932)

¹²⁵ T. Hans and C. E. Raney, U. S. 2,015,796 (Oct. 1, 1935)

¹²⁶ *Paper-Maker* 61: 24 (1946)

¹²⁷ J. F. Maguire and J. G. Rote, *Chem. & Met. Eng.* 48: 163 (1942)

¹²⁸ W. S. Wilson and H. E. Duston, *Paper Trade J.* 117, No. 21: 223–228 (Nov. 18, 1943)

hard water unless a small amount of sodium hydroxide is added to the water to prevent floc formation. Mersize is compatible with rosin size and is almost always used in combination with rosin size.

Mersize plus rosin size is a more effective sizing agent than ordinary rosin size when low percentages of sizing agent are used.¹²⁹ The efficiency of Mersize is due partly to the smaller dimensions of the size precipitate which permits greater coverage of the fibers and partly to the greater number of potential bonds resulting from the multiple carboxyl groups. By itself, Mersize gives poor sizing against water, although it is quite effective against colloidal solutions such as inks or blood.

Ordinarily, Mersize is used to the extent of 10 to 50% of the total weight of sizing agent used. A convenient method of preparing a Mersize and rosin size mixture is to heat and emulsify the rosin size with a steam injector in the regular manner and then to dilute with cold water to a temperature of 100° F. or below, after which the Mersize is then added slowly and stirred until dissolved. More cold water can then be added until the

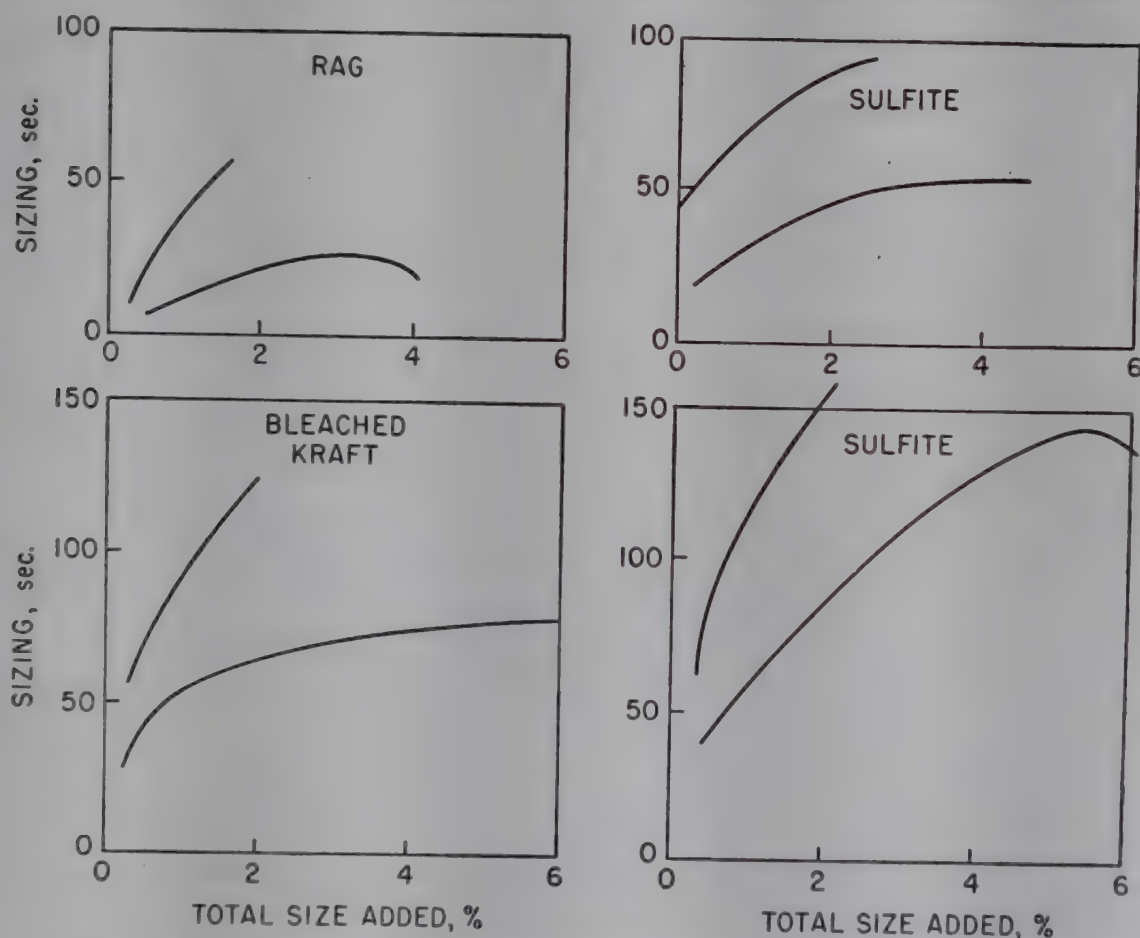


Fig. X-14. Comparison of a Mersize-rosin size mixture with regular rosin size on four different pulps. Upper line in each case represents sizing obtained with Mersize (33 $\frac{1}{3}$ %) plus rosin size (66 $\frac{2}{3}$ %) mixture and lower line represents sizing obtained with rosin size alone.

¹²⁹ W. S. Wilson and H. E. Duston, *Paper Trade J.* 117, No. 21: 223-228 (Nov. 18, 1943)

final concentration is in the neighborhood of 4 to 4.5% total resin solids.

As a rule, the use of Mersize with ordinary rosin size gives maximum sizing at lower percentages of total sizing agent than when rosin size is used alone. The results obtained with a mixture of 33 $\frac{1}{3}$ % Mersize and 66 $\frac{2}{3}$ % rosin size compared with the results obtained with 100% rosin size are shown in Figure X-14 for four different pulps. In every case, the rosin-Mersize mixture produced better sizing. Five per cent alum was used in all cases for setting the size.

Since Mersize is quite expensive, it is advisable to approach the sizing peak with rosin-Mersize mixtures from the low dosage side in order to avoid using dosages greater than needed to give maximum sizing.¹³⁰ Higher percentages of alum are sometimes required with the Mersize than with rosin size because of the greater number of acid groups which provide more bonds for aluminum ions per molecule than is the case with rosin.

Sizing with Bituminous Emulsions

Bituminous emulsions are sometimes added to Fourdrinier and multi-cylinder paperboards. The emulsions are handled like wax emulsions in that they can be mixed directly with the stock and precipitated with alum.¹³¹ They are not used for sizing light-colored stocks, due to the discoloring effects of asphalt. However, asphalt emulsions have been well accepted for the sizing of container and boxboard stocks, structural boards, and for a number of water-resistant specialties where color is not a factor. Between 0.5 to 10% of asphalt solids may be used on the dry fiber weight.

Two types of bituminous emulsions are available: (1) those made with soap alone and (2) those formulated with stabilizing agents, such as clay and glue or casein, to give products which are stable to hard water and metallic salts. The early asphalt emulsions were so stable that they could not be "broken" in the final paper, but since then, improved products have been developed. A desirable product is one in which the emulsified droplets are physically inert and do not stick together or foul the wires and felts of the paper machine, but which tend to flow together and adhere to the fibers when the paper is dried. However, flow should not be so excessive that the particles come to the surface and cause staining. Lorenzini¹³² states that the asphalt in a properly prepared bituminous emulsion is absorbed into the fibers where it retards the penetration of water into the individual fibers.

Sizing with the Silicones

The silicones are organosilicon products containing atoms of silicon

¹³⁰ W. S. Wilson and H. E. Duston, *Paper Trade J.* 117, No. 21: 223-228 (Nov. 18, 1943)

¹³¹ R. H. Cubberly, *Paper Trade J.* 121, No. 12: 111-112 (Sept. 20, 1945)

¹³² E. M. Lorenzini, *Paper Trade J.* 118, No. 21: 180-182 (May 25, 1944)

surrounded by atoms of carbon and oxygen. This group of resins combines the typical properties of inorganic materials with those of the organic synthetic resins. The principal properties are resistance to heat, water, and chemicals. These resins are resistant to temperatures as high as 480 to 570° F.¹³³

The silicones have the interesting property of making paper highly water-resistant when applied in thin films. It is possible, for example, to make a highly water-repellent paper by treating paper with vapor from methylchlorosilane, and this process was utilized during World War II for the manufacture of gas mask filters. The vapor apparently reacts with moisture in the paper to form an extremely thin film of methylpolysiloxane on the surface of the fibers.¹³⁴ The sizing obtained in this way is quite good, but it is necessary to treat the sheet with ammonia vapor to neutralize the acid produced during the reaction.

Bergandohl and Libby¹³⁵ worked with organosilicones of the methylsilicone resin and methylsilicone oil types for beater sizing. They found the

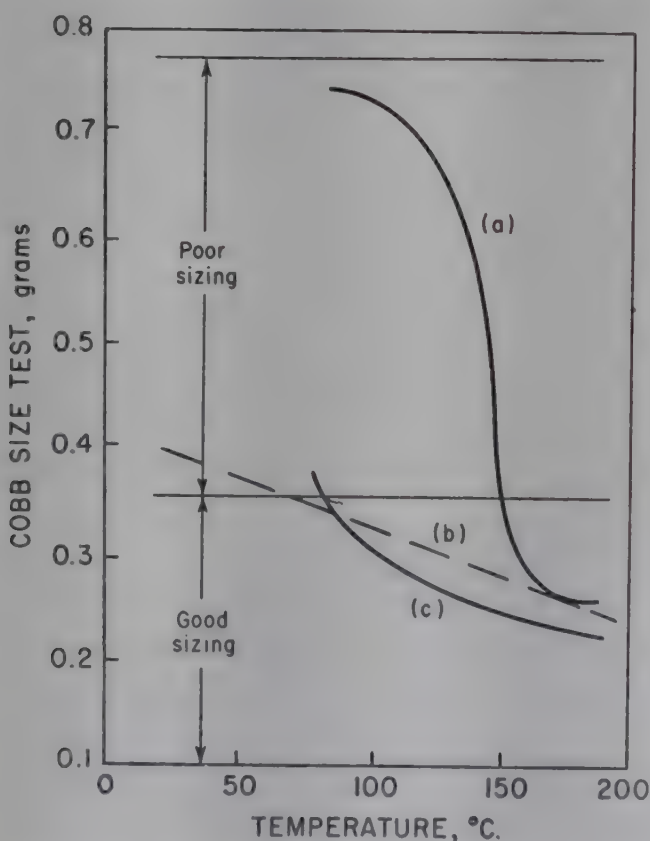


Fig. X-15. Effect of drying temperature on papers sized with silicone resin and methylsilicone oil: (a) 0.5% alkaline emulsion of methylsilicone oil; (b) 0.3% toluene solution of silicone resin; (c) 3.0% neutral rosin.

¹³³ W. T. Eleveth, *Paper Trade J.* 124, No. 22: 122-124 (May 29, 1947)

¹³⁴ Institute of Paper Chemistry, "The Application of Dri-film to Paper," Research Bulletin, Appleton, Wisconsin (Sept., 1945)

¹³⁵ C. J. Bergandohl and C. E. Libby, *Paper Trade J.* 125, No. 10: 108-116 (Sept. 4, 1947)

best product to be a fast-curing silicone resin in a toluene solution and with this product were able to obtain a satisfactory degree of sizing with less than 0.1% resin. They also obtained good results with a mixture of this resin and an alkaline or acidic emulsion of methylsilicone oil, but the silicone oil by itself requires a very high drying temperature, as shown in Figure X-15. Hard water decreases the sizing effect obtained with silicone products.

Pitch Trouble

One of the frequently occurring problems in paper manufacture is pitch trouble, caused by the coagulation of resinous materials and gums on the beater and paper machine parts. This pitch is liberated from the pulp during the beating and refining process and tends to accumulate as a colloidal suspension of negatively charged particles. These particles cause trouble by filling in the wire, thereby producing holes in the finished paper, or by collecting on the felts or machine parts as sticky, dark-colored lumps. The troublesome pitch comes mostly from the resinous matter in the fibers themselves, but in some cases, rosin size causes trouble which is very similar to regular pitch trouble, particularly in mills which have hard water and use an excess of rosin size and alum. Once pitch becomes attached to the machine parts, the only way it can be removed is by scrubbing with gasoline, kerosene, or special cleaning compounds.

Types of Pulps Causing Pitch Trouble

Certain woods, such as jack pine, are much more resinous than others, such as spruce, and consequently are more likely to cause pitch trouble. For example, jack pine may contain up to 3 to 5% resin, compared to 2 to 3% for spruce.

A more important factor than the species of wood is the process by which the wood is cooked. Pitch trouble sometimes occurs with groundwood, but the worst offender by far is unbleached sulfite pulp. Even hardwood pulps may cause pitch trouble if cooked by the sulfite process. The pitch exists in sulfite pulp enclosed in the unbroken epithelial or ray cells, or in the form of a fairly unstable emulsion. The pitch enclosed in the cells causes no trouble so long as the cells remain unbroken.

Soda or sulfate pulps rarely cause pitch trouble, because the alkaline cooking liquor removes most of the resin by saponification during the cooking operation, forming soluble soaps which are removed during the washing of the pulp. This explains why highly resinous woods, such as jack pine, or the Southern pines, which may, in extreme cases, contain as much as 20% resin, do not cause pitch trouble because they are cooked by the sulfate process, and only the young, relatively pitch-free trees are generally used.

It is impossible to determine from an analysis of the pulp whether pitch trouble will occur. Resin in the pulp fibers can be seen by staining the cells with a solution of Sudan III (3 parts alcohol and 1 part water), so that the resin stains orange-red and the fiber remains colorless.¹³⁶ The amount of pitchy substance in the pulp can be determined by extraction first with ether and then with ethyl alcohol but the results obtained are not always indicative of the tendency of the pulp to cause pitch trouble, since pulps of high resin content sometimes cause no trouble and pulps of relatively low resin content sometimes cause serious trouble. Johnson¹³⁷ reports that the portion soluble in naphtha or petroleum ether is the fraction which causes most of the pitch trouble in sulfite pulps. The alcohol-soluble fraction is believed to be far less troublesome.

An evaluation of pulps for their tendency to produce pitch can be made in the laboratory by agitating the pulp suspension at high speed in a metal stirrer and measuring the amount of pitch deposited on the sides of the vessel and on the blades of the stirrer.

Ragan and Kress¹³⁸ point out that a distinguishing characteristic of pitch can be found in its plastic property, since troublesome pitch is generally fluid and tacky, whereas pitch from satisfactory pulp is harder and less mobile.

Effect of Seasoning

The best way to avoid pitch trouble is to season the wood, preferably in chip form, since this greatly speeds up aging. Seasoning oxidizes and polymerizes the pitch in the wood so that it is completely dispersed in the cooking process and does not cause trouble on the paper machine. The generally accepted explanation is that the pitch loses its tacky nature and the small particles do not tend to coalesce into particles of troublesome size. However, it has been reported¹³⁹ that the pitch of seasoned wood is actually stickier than that of unseasoned wood, even though it causes less trouble.

Effect of Cooking, Bleaching, and Washing on Pitch

Overcooked sulfite pulps are more likely to cause pitch trouble than pulps which have not been cooked too long, which can be explained on the basis that the cells in overcooked pulps have been weakened to such an extent that they subsequently rupture and liberate the resin.¹⁴⁰ Pitch trouble is less likely to occur with well-bleached pulps than with unbleached pulps.

¹³⁶ P. Klemm, *Wochbl. Papierfabr.* 42: 967-986 (1911) through *C. A.* 5, No. 18: 3155 (Sept. 20, 1911)

¹³⁷ G. Johnson, *Pulp Paper Mag. Canada* 15: 577-579 (1917)

¹³⁸ R. O. Ragan and O. Kress, *Paper Trade J.* 109, No. 2: 17-19 (July 13, 1939)

¹³⁹ O. Kress and P. E. Nethercut, *Paper Trade J.* 122, No. 26: 289-292 (June 27, 1946)

¹⁴⁰ L. E. Fitzgerald, *Paper Trade J.* 103, No. 17: 266-268 (Oct. 22, 1936)

One means of reducing pitch trouble is to wash the pulp with the warmest water possible, since well-washed pulps generally show less tendency toward pitch trouble than poorly washed pulps. According to Sieber,¹⁴¹ the resin content can be reduced by about 52% by thorough washing. Washing in soft water is preferable. Extraction of the pulp with organic solvents in which the pitch is soluble has been suggested, but this method is too expensive for practical use.

Because most of the pitchy material exists in the ray and epithelial cells, methods have been suggested for removing these small cells from the pulp by screening. In this connection, Edge¹⁴² found that a removal of 2% of these fiber fines by screening reduced the pitch content of the pulp by 20 to 50%.

Effect of Machine Conditions on Pitch Trouble

The temperature of the stock on the paper machine is quite important in controlling pitch trouble. Kress and Moss¹⁴³ found that no deposits occurred with rosin size until the temperature of the suspension approached the melting point of the rosin. Too much recirculation of white water should be avoided, since this water contains a preponderance of the fine cells which are the source of pitch trouble.

Effect of Added Materials on Pitch Trouble

One way of correcting pitch trouble is to add materials to the paper stock such as bentonite or diatomaceous silica, which coat or absorb the individual particles of pitch and prevent them from sticking to each other or to parts of the paper machine. In practice, about 5 to 20 lb. of bentonite or diatomaceous silica are added per 1,000 lb. of stock. Generally, the material is added as early as possible in the beating period, although in some cases best results are obtained by adding about fifteen to thirty minutes before dropping the beater load. Late addition of diatomaceous silica is advantageous when large amounts of rosin size or starch are used in order to minimize clogging of the pores of the silica particles.

Materials such as starch, animal glue, and gelatin have also been suggested as remedies for pitch trouble, since these materials act as protective colloids and tend to prevent agglomeration of the resin particles. Special dispersing agents, e.g., the sodium salt of condensed naphthalene sulfonic acids, have also been used for controlling pitch. These reduce the amount of pitch deposited and reduce the tackiness of the pitch. Adding sodium hexametaphosphate (calgon) to the water in an amount of 0.05 to 0.50%

¹⁴¹ R. Sieber, *Papier-Fabr.* 13: 389 (1915)

¹⁴² S. R. H. Edge, *World's Paper Trade Rev.* 102, No. 16: 1184-1186, 1188, 1230-1232; No. 17: 1262, 1300 (Oct. 19, 26, 1934)

¹⁴³ O. Kress and L. A. Moss, *Paper Trade J.* 102, No. 25: 38-49 (June 18, 1936)

of the weight of the stock is claimed to reduce pitch troubles.^{144, 145} The effect is not very great in the case of sulfite pulps, but is appreciable in the case of groundwood pulps.

An alkaline medium containing calcium ions is a situation highly conducive to the formation of pitch,¹⁴⁶ and thus, alkaline fillers (e.g., calcium carbonate) tend to aggravate pitch troubles.¹⁴⁷ According to Gavelin,^{148, 149} bicarbonate ion is principally responsible for pitch trouble, possibly because the liberated pitch tends to accumulate in the foam produced by bubbles of carbon dioxide. Lowering the pH of the pulp suspension reduces pitch trouble, and for this purpose, alum is considerably more effective than acids.

¹⁴⁴ H. A. Freeman, *Pulp Paper Mag. Canada* 48, No. 8: 73-75 (July, 1947)

¹⁴⁵ G. Gavelin, *Pulp Paper Mag. Canada* 50, No. 10: 109-115 (Sept., 1949)

¹⁴⁶ K. Stahlberg, *Svensk Papperstidn.* 42, No. 16: 408-412 (Aug. 31, 1939)

¹⁴⁷ H. R. Davidson, *Pulp Paper Mag. Canada* 46, No. 3: 205-211, Sixth Wartime Issue (1945)

¹⁴⁸ G. Gavelin, *Pulp Paper Mag. Canada* 51, No. 5: 87-89 (Apr., 1950)

¹⁴⁹ G. Gavelin, *Pulp Paper Mag. Canada* 50, No. 2: 59-64 (Feb., 1949)

SURFACE SIZING

In the last chapter, internal sizing was discussed. In this chapter, a different form of sizing, known as surface sizing, is described.

Effect of Surface Sizing on the Properties of Paper

Surface sizing differs from internal sizing in that the sizing agent, e.g., animal glue or starch, is applied to the surface of the paper where it cements the fibers to the body of the paper and deposits a more or less continuous film on the paper surface. The advantage of surface sizing is that a smooth hard film is produced on the surface of the paper which will not catch the pen when the paper is written upon and will not pick if the paper is printed with tacky inks. Furthermore, the oil resistance of the paper is increased, since the surface pores of the paper are sealed. Surface sizing is oftentimes more important than internal sizing for writing papers, printing papers, and certain grades of wrapping papers.

Types of Surface-Sizing Agents Used

The two principal surface-sizing agents used commercially are starch and animal glue, starch being used to the greatest extent. Other sizing agents, including methylcellulose, carboxymethylcellulose, polyvinyl alcohol, and wax emulsions, are sometimes used to obtain special effects. Surface-sizing agents can be applied in a size press, in a size tub, or (in the case of heavy papers) at the calenders. The various methods of applying surface-sizing agents will be discussed later in this chapter.

Surface sizing is primarily concerned with surface films, and consequently it is usually desirable to keep the size on the surface of the paper as much as possible, where it will do the most good. This is particularly true when using expensive sizing agents such as polyvinyl alcohol, carboxymethylcellulose, and even animal glue. On the other hand, it is desirable on some grades of paper, when starch is the sizing agent, to obtain considerable penetration of starch into the paper in order to build up the burst, internal sizing, and other internal properties of the sheet. Lee^{1, 2}

¹ H. N. Lee, *Paper Trade J.* 107, No. 6: 53-59 (Aug. 11, 1938)

² H. N. Lee, *Paper Ind.* 19, No. 7: 785-794 (Oct., 1937)

has shown that commercial papers surface-sized with starch vary from papers showing very little penetration of starch to papers where the starch has penetrated completely through the sheet.

Surface-sized papers should not be visualized as having a continuous film covering the entire surface, because this condition is rarely attained. Lee^{3, 4} has noted that starch covers the surface fibers very irregularly, being thin in some spots and dense in others, so that a continuous film is not obtained unless a high concentration of starch is applied. Most commercial papers surface-sized with starch have a somewhat uneven, discontinuous film of starch on their surface. Animal glue appears to form a better film than starch, but as a rule it, too, does not form a completely unbroken film, although in rare cases a uniform, fairly continuous film may be obtained.⁵ On the other hand, some of the better film-forming substances, such as polyvinyl alcohol, zein, methylcellulose, and carboxymethylcellulose tend to produce a sizing layer which more nearly approaches a continuous film. The film of sizing agent is, however, often broken by the presence of fibers protruding from the surface of the sheet.

Effect of Surface Sizing on Water Resistance

Surface sizing with starch does not materially increase the water resistance of the paper, and even with animal glue there is only a slight increase in the water resistance. The low water resistance of these materials is due to their low angle of contact with water. However, water resistance is not particularly desired in surface sizing, since the primary purpose of the size is to make the paper resistant to colloidal solutions (writing inks) or to oily vehicles (printing inks). It should be pointed out that two papers with the same internal sizing (as measured by the water penetration test) may differ greatly in surface sizing (as measured by the writing qualities of the paper).

Papers to be printed by the offset process are usually surface-sized with starch in order to prevent the loosening of surface fibers during moistening of the paper with water on the press. According to Cobb,⁶ surface films of starch increase the sensitivity of offset papers to changes in the relative humidity of the atmosphere, but starch-sized papers are useful for offset printing because it is possible, by sizing with starch, to use stock which has been beaten to a lesser degree. In this way, advantage is taken of the functional properties of the starch film which produces a hard, slightly water-resistant surface over a softer, freer body stock.

A number of other special grades of paper are surface-sized com-

³ H. N. Lee, *Paper Trade J.* 107, No. 6: 53-59 (Aug. 11, 1938)

⁴ H. N. Lee, *Paper Ind.* 19, No. 7: 785-794 (Oct., 1937)

⁵ H. N. Lee, *Paper Trade J.* 107, No. 6: 53-59 (Aug. 11, 1938)

⁶ R. M. Cobb, *Paper Trade J.* 100, No. 16: 200-204 (Apr. 18, 1935)

mercially for special or unusual effects. One special case which might be mentioned is the surface treatment of paper with starch or glue to produce alkali-proof papers for use as soap wrappers. In this application, the sizing prevents the alkali in the soap from discoloring the paper or destroying the rosin in the sheet.⁷ The degree of protection required depends upon the amount of free alkali and the moisture content of the soap. Low iron content in the paper is important in preventing discoloration.

Effect of Surface Sizing on Penetration of Oils

The penetration of oils into paper is important in papers to be printed with high gloss inks, papers to be coated with paraffin, or papers to be used in contact with greasy foods. The most oil-resistant papers are those papers of very low porosity (glassine and greaseproof papers), or those papers which have been surface sized with a film of oil-resistant material. Surface sizing with starch, animal glue, carboxymethylcellulose, polyvinyl alcohol, or similar materials is used commercially for producing papers which must be resistant to oily materials. These sizing agents are effective because they increase the contact angle against oil and provide a relatively non-porous film through which the oil cannot penetrate.

The oil resistance of paper is generally measured by the time required for an oily test liquid to penetrate through the paper. For best results, the paper should be tested against the material with which it comes into contact during use, but in many cases turpentine is used to speed up the test. The standard turpentine test is based upon the time required for water-free turpentine to penetrate through the test specimen and discolor an underlying sheet of book paper. In carrying out this test, 1.1 ml. of turpentine (which has been colored red with an oil-soluble dye) is added to a pile of sand (5 g.) on top of the test specimen, and the time is taken for complete penetration through the paper.

The results of such tests as the turpentine test do not correlate well with the resistance of the paper to oily materials of high viscosity, e.g., printing inks. This is shown in Figure XI-1,⁸ where the resistance to the penetration of oils of varying viscosity is shown for papers surface-sized with different amounts of carboxymethylcellulose. It can be seen from these results that it is possible to have a considerable difference in oil resistance between samples when tested with high-viscosity oils, but little difference when tested with low-viscosity oils. The amount of moisture present in the test liquid affects the rate of oil penetration, although the initial penetration may not be greatly changed.⁹

⁷ A. A. McAneny, *Graphic Arts Monthly* 12, No. 9: 50-54 (Sept., 1940)

⁸ E. F. Horsey, *Tech. Assoc. Papers* 30: 294-298 (June, 1947)

⁹ *Tappi* 32, No. 5: 200 (May, 1949)

The degree of oil resistance required in commercial papers depends upon the end use of the paper. Greaseproof wrapping papers require a high degree of oil resistance and hence must be surface-sized so that there is a rather heavy, continuous film of sizing agent on the surface of the paper.

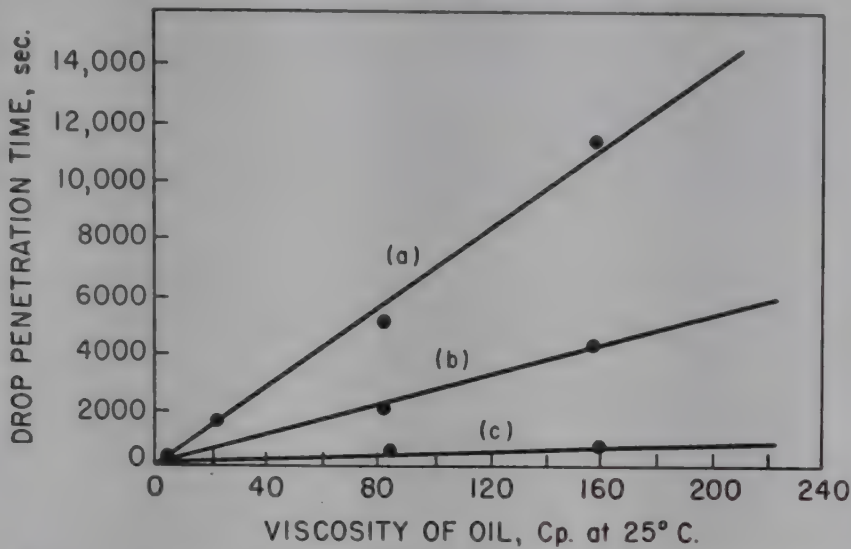


Fig. XI-1. Effect of viscosity of oil on the oil resistance of papers surface-sized with carboxymethylcellulose: (a) 2% solution applied at size press and 4% applied at calenders; (b) 4% solution applied at calenders; (c) no surface treatment.

These papers are often folded and creased during use, and consequently it is desirable to make the tests on creased samples to determine the flexibility of the film. Fats (e.g., Crisco) may be used for testing, either by determining the time required for the complete penetration of the melted fat through the paper (thin paper) or by determining the weight of the melted fat absorbed by the paper (heavy paper).

When surface sizing is used for improving the printing properties, as in the sizing of paperboard for gloss ink printing, there are definite limitations to the amount of sizing agent to be applied, since the surface absorbency of the paper must fall within definite limits, depending upon the type of ink used and the results desired in the printed paper. If too little surface size is used, the paper will absorb too much ink during printing, thereby producing a flat, unattractive printing job. On the other hand, if there is too much surface size, the ink will be slow in drying, resulting in "offset" and shiny spots.

Effect of Surface Sizing on Writing Qualities

The writing qualities of paper with ink are of great importance on such grades as bond, ledger, tablet, envelope, papeterie, index bristol, chart paper, and business forms, since these grades are generally written upon with pen and ink. Another grade requiring the same general qualities is paper for commercial ruling. This paper is purchased by manufacturers of blank

books or stationers and is ruled with a disk ruler (for tablets and exercise books) or with a pen ruler (for ledgers or similar books requiring multi-colored or discontinuous lines).

The better grades of the above papers are surface-sized, generally with starch or animal glue. Surface sizing improves the writing qualities because of the effect in increasing the contact angle,^{10, 11} increasing the smoothness, and reducing the porosity of the paper. The sizing agent acts as a film which "filters out" the dyestuffs in ordinary writing ink, thereby preventing "feathering" or spreading of the ink particles over the surface of the paper.

The writing qualities of paper are determined to a large extent by the type of ink used. The earliest inks were made from the juice of colored berries, and later from simple suspensions of carbon black in water with some gum or gelatin added to prevent feathering of the ink on the paper. The iron tannate inks were developed in the twelfth century and were first made from ferrous sulfate, tannin from nutgalls, and some glue or vegetable gum. These inks contain soluble ferrous-tannin compounds which are converted into insoluble ferric compounds upon exposure of the ink line to air. The dye-base inks were developed later to produce an ink which would keep indefinitely in the bottle and not form thick deposits. These inks are less permanent than other types, and for this reason, iron salts or colored metal oxides are sometimes added to provide coloring matter which exists after the organic dyestuff has faded. Record inks are a special type which are made slow-drying by the addition of glycerine. Direct dyestuffs are used in these inks because they feather less than acid or basic dyestuffs. With the development of the fountain pen, it became necessary to eliminate gum arabic and other gums from the ink, and even, in some cases, to add surface-active and hygroscopic agents in order to keep the ink free-flowing in the pen.¹² Modern, quick-drying inks, which dry within a few seconds after application to the paper, dry either through evaporation of the solvent or through penetration of the vehicle into the paper. Most of these inks contain a small amount of a non-volatile, water-miscible, surface-active agent to promote penetration of the ink into the paper. These agents have the disadvantage that they increase the horizontal penetration, as well as the vertical penetration, thus causing feathering.¹³ The type of ink developed for use in ball point pens is a non-aqueous ink and can be used for writing on unsized papers.

The writing qualities of paper are generally measured by a simple test, termed the "pen and ink" test, which is carried out by drawing several lines

¹⁰ G. H. Lafontaine, *Paper Trade J.* 113, No. 6: 63-66 (Aug. 7, 1941)

¹¹ J. E. Foote, *Paper Trade J.* 109, No. 14: 182 (Oct. 5, 1939)

¹² B. W. Smith, *Paper Trade J.* 120, No. 8: 72-73 (Feb. 22, 1945)

¹³ W. B. Reynolds, *Chem. Eng. News* 916-918 (Apr. 10, 1946)

on the paper in one direction and several in the opposite direction, using an ordinary draftsman's pen or a special pen (silver alloy pen No. 225). It is best to test the paper against the particular type or types of ink with which it is to be used, although often a standard writing ink or, in some cases, a 0.08% solution of Malachite green is used. Lack of good writing quality is manifested in these tests by feathering or spreading of the ink particles into the fibers beyond the points of contact of the pen. The sizing should be tested on both sides of the sheet, since in many cases the writing qualities may be satisfactory on the felt side and unsatisfactory on the wire side.

The most common paper complaints in pen ruling result from defects in the paper surface.¹⁴ A common defect, which contributes to skipping and broken lines by causing the pens to fill with fuzz and lint, is loosely bound surface fibers, but this difficulty can be eliminated by satisfactory surface sizing of the paper. Another difficulty is rough surface arising from felt marks, wire marks, watermarks, or press roll marks. Greasy spots on the surface of the paper resulting from too much grease in animal glue surface size causes trouble with skipping, as does also the presence of slime spots. Excessive filler content in the paper causes excessive wear on the ruling pens, especially when abrasive fillers are used. The moisture content of the paper at the time of ruling is an important factor; a change in the relative humidity of the atmosphere in which the paper is stored from 20 to 85% may double the amount of ink spread or feathering¹⁵ or, in other words, change the paper from the fair class into the very poor class. The dimensions of the fibers and the amount of machine to cross direction alignment affect the ruling qualities. Best results are obtained in commercial ruling, which is usually carried out in one direction only, when the lines run parallel to the fibers. In general, the ruling and writing qualities of rag papers are superior to those of sulfite or groundwood papers.¹⁶

Effect of Surface Sizing on Erasability

Erasability may be defined as that property of paper which permits writing to be removed from the paper by erasure and which prevents excessive erosion of the paper by erasure. Paper of good erasability should also maintain a satisfactory appearance when the erased area is written upon again. Thus, the erasability is really a composite of the resistance of the paper to the penetration of ink, resistance of the paper to abrasion, ability of the paper to maintain a smooth surface, and ability of the paper to retain sizing value after erasure.

¹⁴ F. S. Klein, *Paper Trade J.* 120, No. 14: 131-133 (Apr. 5, 1945)

¹⁵ M. O. Schur and R. M. Levy, *Paper Trade J.* 122, No. 12: 121-125 (Mar. 21, 1946)

¹⁶ W. S. Wilson, *Paper Trade J.* 123, No. 24: 198-202 (Dec. 12, 1946)

The erasing qualities of paper are important for such grades as ledgers, bonds, stationery, and drawing tablet, because such papers must permit writing over erased areas. These papers require a high degree of internal sizing and, also, for the best grades, a surface sizing with animal glue or starch.

The ease of erasure can be determined only after the paper has been written or printed upon with the appropriate ink, inasmuch as the erasing qualities are, to a considerable extent, related to the writing and printing qualities of the paper. There may be quite a difference between the erasing qualities of a given paper when printed with an oil-base ink compared with those of the paper when written upon with a water-base ink. The ease of erasure may be measured by such simple methods as scraping the written area with a knife or rubbing the paper with erasing rubbers of different hardness. More elaborate tests involve the use of mechanical abrading machines such as the Taber abrader (see Ch. XVI). The results of the test should indicate in some way the amount of abrasion required to erase the written matter from the paper, as well as the amount of abrasion the paper will stand without feathering when the erased area is written upon.

Most commercial papers requiring a high degree of erasability are surface-sized with starch or animal glue. Surface sizing improves the erasability of paper in two ways, by reducing the penetration of ink into the paper, thus making it easier to remove the ink by erasure, and by increasing the fiber bonding, thus increasing the resistance of the fibers to abrasion. The extent of penetration of the sizing agent into the paper during the surface sizing operation is an important factor, since a light surface film of size without much penetration may furnish an initial high resistance to erasure, but the paper may not hold up under repeated erasure. The ideal condition is to have a fairly heavy surface film of sizing agent to provide high initial erasability, and a strong, well-sized body stock which will hold up under repeated erasure.

The erasability of paper can be studied by mechanical abrasion tests, results of which are shown in Figure XI-2, where the weight loss obtained for different papers on the Taber abrader is plotted against the number of wear cycles.¹⁷ As can be seen from these curves, unsized book paper loses weight by abrasion in a straight line relationship with the number of wear cycles, and the loss in weight is very rapid. The surface-sized papers, on the other hand, lose weight slowly up to a certain point, after which the curves break suddenly and the weight loss increases much more rapidly. This break in the curve probably corresponds to the point where the abrasive wheel breaks through the surface film of size into the interior of the

¹⁷ Unpublished work of C. R. Ward on "The Effect of Surface-Sizing Agents on the Erasability of Paper," New York State College of Forestry, Syracuse, N. Y. (May 20, 1950)

paper. In most cases, the sheet feathers upon rewriting shortly after the break-through point, although one sample was strong enough internally to resist considerable more abrasion before showing evidence of feathering. The results reported in Figure XI-2 are for commercial grades of writing

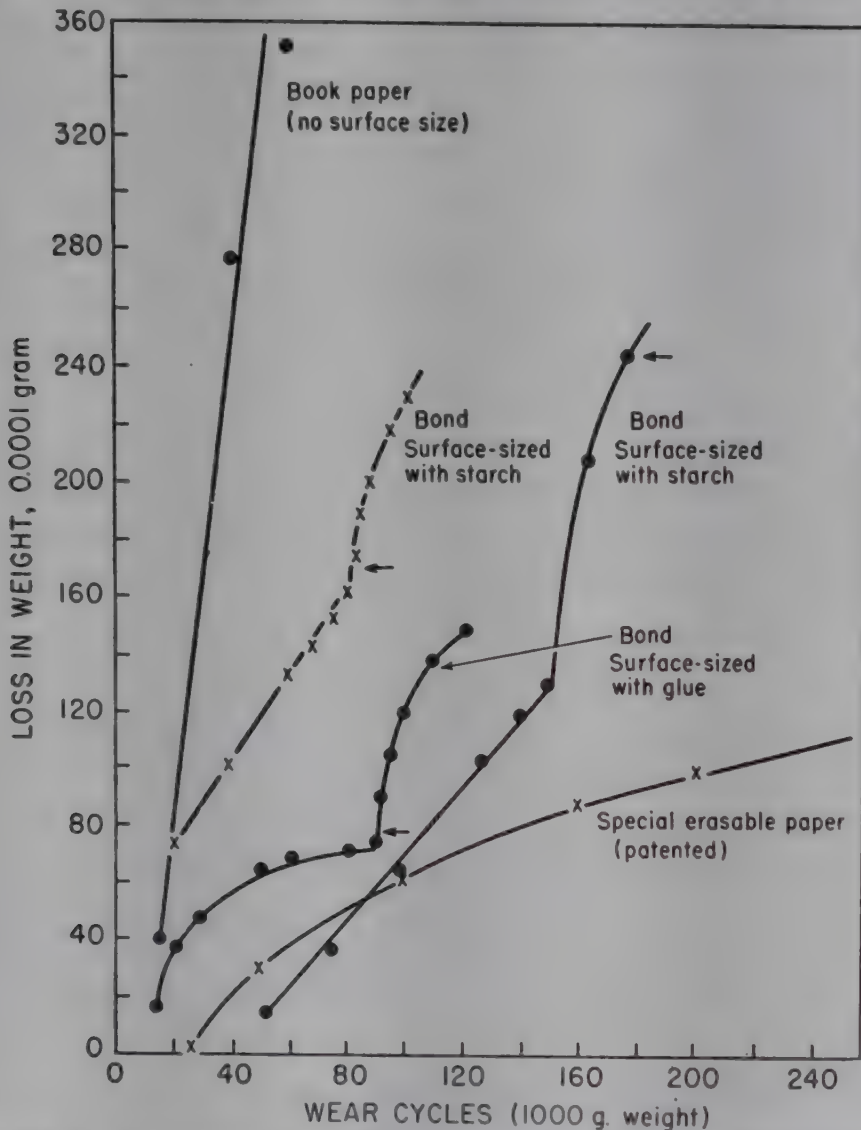


Fig. XI-2. Erasability tests (Taber abrader) on various commercial papers. Arrows (\leftarrow) indicate point of first feathering.

papers manufactured especially for high erasability. Another grade of commercial paper of exceptionally high erasability is also shown. This special grade of erasing paper is made by a patented process¹⁸ in which the paper is coated with casein, starch, or glue to produce an even surface layer of about one-tenth of a mil in thickness which follows the surface contour of the paper. This film of coating is intentionally made fragile enough to rupture under the impact of the type on a typewriter. This forms an impression which is readily erasable at first, but which slowly penetrates through the broken layer of coating into the interior of the paper, thus progressively forming a more indelible impression. As can be seen from

¹⁸ J. G. Callan, U. S. 1,994,750 (Mar. 19, 1935)

Figure XI-2, the erasing test on this grade of paper showed only a very gradual loss in weight, and there was no break in the curve and no feathering up to 1,000 wear cycles.

Effect of Surface Sizing on Physical Properties

In addition to improved sizing value, surface sizing agents also have an effect on the strength of the paper. Usually there is enough penetration of sizing agent into the paper to increase the fiber bonding and the dependent properties, such as bursting, tensile, and folding strengths. An additional effect, which results from a cementing of fibers to the body of the sheet, is an improvement in the scuffing resistance of the paper surface.

Surface Sizing Processes

In the following sections, some of the surface-sizing processes are discussed. In general, surface sizing on the paper machine is done by any one of three different processes, which include sizing by means of a size press, sizing by means of a size tub, or calender sizing. All three are discussed below.

Surface Sizing with Size Press

Paper is commonly surface-sized on the paper machine by means of a size press whereby the sizing agent is applied to both sides of the paper and the paper is then passed through press rolls to drive the size into the paper and remove the excess size from the surface of the paper. In most cases, the size (usually starch) is sprayed onto the paper so that the paper runs through a puddle just before entering the nip of the rolls. The paper is in contact with the size for only a short period of time, and the pick-up of size is relatively low.

The size press consists of two rolls, top and bottom. The top size press roll is usually a dead hard rubber-covered roll, a Stonite roll, or a brass roll. The bottom roll of the size press is a softer rubber-covered roll (usually a 20 plastometer, although densities up to 40 are used). The hardness of the rubber-covered roll determines the amount of pick-up of size. There are two instruments used for measuring the hardness of the rubber, the plastometer¹⁹ and the densimeter, the plastometer reading is twice the densimeter reading.

The angle at which the paper enters the nip of the press rolls determines the area of the "puddle" on the top side of the sheet. Lowering the sheet entering the press increases the area of the puddle and hence increases the pick-up of size. The pressure used on the rolls can be regulated (either by weights or by a pneumatic roll loader) to drive more or less size into the

¹⁹ The Pusey and Jones Plastometer shows the depression of the rubber surface caused by a $\frac{1}{8}$ -in. ball needle under a 1-kg. weight applied slowly.

paper. A pressure recorder is desirable in order to permit accurate duplication of pressure on different runs. The condition of the rolls is of the utmost importance in the operation of a size press, and these should be ground to a very smooth surface and kept in good condition by regrinding when necessary. The pressing should be as uniform as possible across the width of the machine, since otherwise, wet streaks in the sheet will result. Certain papers surface-sized with starch in a size press appear uniformly sized, but take on all kinds of peculiar designs when soaked in water or stained with dilute iodine solution. What happens is that the partially dried sheet, which is very soft after treatment with the size, is expanded laterally under the pressure at the nip so that, upon leaving the nip, the sheet immediately contracts and forms puckers which tend to wipe more starch from the top press roll. This occurs only on fairly light-weight sheets and can be corrected by increasing the draw or tension on the paper.

The crown of the press rolls is another important factor. If the crown is too great, the sheet will be tight in the center and loose at the edges on coming out of the press. If there is too little crown, the sheet will be loose and baggy in the center. The correct crown is usually a compromise, since the correct crown for a heavy sheet will not be the most satisfactory crown for a light sheet. The crown is determined by previous experience, since there is no known mathematical formula for accurately determining crown. The proper crown can be verified by making moisture determinations across the width of the sheet after the press. In most mills, the top size press roll has a straight face (no crown), whereas the bottom roll has a crown which varies with the diameter, face and deflection of the roll. Some examples of crowns used on bottom size press rolls are listed below:

Finished diameter, in.	Face, in.	Diameter of crown, in.
16	86	0.012
21	130	0.015
24	157	0.040
28	180	0.050

After the sheet leaves the press, it is passed over a spread roll to remove wrinkles. The angle at which the sheet passes over this roll and the distance between this roll and the press are important factors in the operation of a size press.²⁰ As a rule, there are six to eight drier rolls after the size press which are used to drive out the moisture picked up by the paper.

Surface Sizing with Size Tub

Another method of surface sizing utilizes a tub for holding the size into which the sheet is dipped. The time of contact of the paper with the

²⁰ J. H. Miller, *Paper Ind.* 28, No. 7: 973-974 (Oct., 1947)

size depends upon the speed of the machine, the dimensions of the tub, and the area of the sheet submerged in the size at one time. Usually the size tub is located within the drier section so that the sheet is partially dried before reaching the tub. Drying of the sized paper is completed by passing the paper over six to eight driers. Some machines are equipped with tension indicators and regulators to prevent undue stretching and weakening of the sheet in the tub.

The use of size tubs is older than the use of the size press, and many companies have replaced their tubs with presses because the latter are easier to operate, cleaner, and subject to more control. On the other hand, the size tub results in longer contact of the paper with the size, and results in about 25% more size being picked up by the paper. For this reason, some of the high-grade rag mills still use size tubs.

Surface Sizing off the Machine

In addition to the above two sizing processes which are carried out on the paper machine, special grades of paper may be surface-sized in a separate operation off the machine. Wet soak or wet pack paper is a special grade of surface-sized paper which is made by tub sizing the sheet in a separate unit equipped with sizing tub and driers. In this process, the paper, immediately after sizing, is wet-wound while it still contains about 35% moisture. The wet paper is then allowed to stand for several hours to obtain greater and more uniform penetration of size. At the end of this period, the paper is usually passed through special air driers to remove the moisture.

Special sizing processes may also be used, such as one involving the deposition of a thin film of silicone resin on the surface of the paper by passing the paper through a chamber containing silicone resin vapor. This process is mentioned to illustrate what might be done, since it is not a regular commercial process.

Calender Sizing

Calender sizing is another important method of applying size to the surface of paper on the paper machine. This method of sizing is used only with heavy papers such as paperboard, since by and large, light-weight papers are sized with a size press where the treatment can be followed by drying. The reason that it is possible to size heavy papers at the calenders without supplementary drying is that the board, when it reaches the stack, carries a considerable amount of latent heat which permits some evaporation of water before winding. The water which remains can be absorbed throughout the entire mass of the board without any appreciable increase in the overall moisture content. Calender sizing is very largely a surface phenomenon, and no particular advantage, from a sizing standpoint, is

gained in having size distributed throughout the entire board, although this gives some strength improvement.

Factors Affecting Surface Sizing

To insure picking up a uniform amount of size, the sheet going to the size press or size tub should be uniform in regard to moisture content, internal sizing, and density. Furthermore, the size solution itself should be uniform as to concentration of sizing agent, viscosity, and temperature. Some of the important factors are discussed below.

Sizing tests made on the paper previous to the size press and immediately after the size press are of value in indicating the percentage of the total sizing value which is the result of the internal and surface sizing operations.

Effect of Sheet Moisture Content

There is an ideal moisture content to insure picking up the optimum amount of size by the paper, and the general opinion of operating men is that this ranges from 4 to 12%, with the majority advocating from 8 to 12%. A sheet which is wetter or dryer than the optimum will not pick up the maximum amount of size. If the sheet is relatively dry before entering the size, it will come out wider as the fibers readjust themselves in dimensions.

The results in Table I, which were obtained in a commercial run on offset paper using starch at the size press, show the effect of changes in moisture content of the paper going to the size press on the physical properties of the final paper. These results show that the paper is increased in strength and sizing value, on account of an increase in the pick-up of size, as the moisture content is increased up to at least 7%. If the moisture content is too high, the sheet tends to sag upon entering the press and any lumps in the sheet entering the press will result in a hole.

To maintain uniformity in the sizing operation, the data in Table I indicate the necessity of automatic moisture control of the paper entering

TABLE I

EFFECT OF MOISTURE CONTENT OF PAPER ENTERING SIZE PRESS
ON THE PROPERTIES OF THE SIZED PAPER

Moisture in paper entering size press, %	Ink penetra- tion, seconds	Dennison wax test		Burst
		Wire side	Felt side	
2.3	215	17	11	26.0
4.6	350	18	11	26.5
6.3	575	19	11	26.5
7.5	530	19	12	30.0

the size press or size tub. Equipment which automatically maintains a constant temperature in the drying section is of considerable aid, but these installations require manual adjustment of temperature from time to time. Far more satisfactory results are obtained when continuous moisture recorders are used to control automatically the temperature in the drier section so that the sheet maintains a constant moisture content.

Effect of Internal Sizing

A definite relationship exists between the internal sizing of the paper and the amount of size pick-up in the surface sizing operation. During World War II when rosin was difficult to obtain, many mills were able to maintain a satisfactory degree of sizing by reducing their internal sizing and increasing their pick-up of starch in the size tub and size press. The figures in Table II show in an approximate way how the pick-up of surface size varies with the internal sizing of the paper. These results are for size tub operation and somewhat lower values would be expected for size press operation.

TABLE II

EFFECT OF INTERNAL SIZING ON THE PICK-UP OF SURFACE SIZE

	1	2	3	4
Internal sizing, % rosin size	0	0.5	1.0	2.0
Pick-up of size, % size on paper air dry basis	10	9	7	5

The ratio of internal sizing to surface sizing depends somewhat upon the type of paper being made. Pattison²¹ prefers a slight feather in the paper before the size tub when making cotton cockle bond in order to insure absorption of sufficient size to obtain good cockle. On the other hand, he prefers hard internal sizing before the size tub when making offset paper in order to keep the size on the surface of the paper. However, even for offset papers there must be sufficient penetration of size into the interior of the paper to strengthen the fiber bonding (see offset papers in Chapter XIX).

The electrocapillary effects, which have their basis in the electrostatic charges on the fibers in the pores of the paper, influence the results of surface sizing with starch or animal glue. In this connection, Rowland and Harrison²² found, by using colloidal alumina to change the charge on the fibers at will, that negatively charged fibers tend to repel starch and that positively charged fibers tend to precipitate the starch and plug the pores

²¹ R. W. Pattison, *Paper Trade J.* 129, No. 21: 450 (Nov. 17, 1949)

²² B. W. Rowland and J. J. Harrison, *Paper Trade J.* 119, No. 20: 199-203 (Nov. 16, 1944)

of the paper. Thus, either a highly negative or a highly positive condition of the fibers tends to inhibit the penetration of starch. Starch penetrates more readily when the sheet is negatively charged than it does when the sheet contains an excess of positively charged alumina, but only near the neutral point does starch penetrate freely.

Effect of Sheet Density and Smoothness

The density has an important effect on the penetration of surface size, since high-density papers pick up less size than porous papers. The density of the paper is also a factor in the overall sizing value, as previously explained. In highly porous papers the size replaces air in the sheet and this air is absorbed by the size, thus contributing to foaming troubles.

It is important that the surface of the paper before sizing be as smooth and as free from fuzz as possible. If the sheet is fuzzy, the final paper will contain bare fibers protruding above the surface, regardless of how much size is applied. These fibers will serve as wicks for the conduction of water or other liquids through the surface film into the body of the paper, thereby defeating the purpose of sizing. Under adverse conditions, the paper may show feathering beneath the surface of the size when written upon with ink.²³

The sizing value is related to the finish of the paper surface. As a general rule, surfaces with a positive wetting tendency will wet more readily the rougher the surface, and, conversely, surfaces with a negative wetting tendency become more water-repellent the rougher the surface.²⁴ This explains why machine-finished papers with a relatively grainy surface usually show a higher contact angle with water than highly calendered papers. For the same reason, sizing agents which are ineffective on smooth surfaces may show excellent water-repellent properties when applied to fibrous surfaces.²⁴

Effect of Viscosity and Temperature of the Size

The properties of the size itself are of the utmost importance in determining the amount of penetration of size into the paper. The equation of Cobb²⁶, given earlier, shows that the important properties of the size solution are surface tension, wetting properties, and viscosity. The time of exposure of the paper to the size solution and the concentration of the solution are the remaining important variables.

Of particular importance in determining the amount of size penetration

²³ "Report of Paper Testing Committee on Sizing," *Paper-Maker* 114, No. 3: 22-28 (Sept., 1947)

²⁴ R. N. Wenzel, *Ind. Eng. Chem.* 28, No. 8: 988-994 (Aug., 1936)

²⁶ R. M. Cobb, D. V. Lowe, E. Pohl and W. Weiss, *Paper Trade J.* 105, No. 7: 33-36 (Aug. 12, 1937)

is the viscosity, since the penetration varies inversely as the square root of the viscosity of the solution. For this reason, the viscosity of the sizing solution should be regulated with considerable care to obtain the proper penetration for the grade of paper being made. Two very important practical considerations in surface sizing are the concentration and the temperature of the size, since these variables are not only important by themselves but also determine the viscosity of the solution. Instruments for the automatic control of temperature and Baumé of the size at the size tub have been developed and are in successful operation at present. Instrumentation in this operation is extremely helpful in attaining uniform, satisfactory results.

The temperature of the size used in a size press has a practical upper limit imposed by that which the rubber-covered press rolls can stand without checking. Also, in cases when the paper dips into the size and no automatic feeding devices are in use, it is very difficult to feed the paper manually at temperatures above 125 to 130° F., and this imposes a limit on operating temperature. If the size tub temperature is not controlled automatically nor adjusted manually, an equilibrium temperature is attained after a period of continuous operation, since the hot paper entering the size continually adds heat. The equilibrium which is established depends upon the temperature of the paper and the machine speed.

Effect of Drying and Calendering

Careful drying is important in surface sizing. Most surface-sized paper is dried on the paper machine under rather adverse conditions. Some glue-sized papers are packed in a wet condition and then are dried slowly in an air drier at relatively low temperature. This produces much contraction and cockling of the paper, but results in the fullest benefits in the way of strength and sizing.

Too rapid drying results in cracking and checking of the surface film. Another trouble which may occur if drying conditions are not right is a picking or flaking off of the surface film of size on the driers. Poor results due to improper drying may be corrected by remoistening the sheet and drying again under more favorable conditions, but this is an expensive procedure. Flaking of the sized paper during drying may be prevented by operating the first driers at low temperature and by covering with copper and stainless steel.

The amount and type of calendering is important because excessive calendering tends to drive the surface film of size into the paper, thus breaking the continuity of the film. This is likely to occur if the calendering is done while the sheet has too high a moisture content. In some cases, picking of the surface size occurs on the calenders.

Surface Sizing with Starch

Considerable starch is used for surface sizing. Starch is much cheaper than animal glue and has replaced it as a surface size on all but the highest grades of papers. Most of the starch used in the United States is derived from corn, although a large amount of tapioca starch has also been used. Potato starches are also being used.

General Properties of Starch for Surface Sizing

Starch is a white- to buff-colored material which is sold in powdered, pearl, or crystal form. Starch exists in the physical form of small grains or granules, the size, shape, and physical markings of which are sufficient to identify the variety of starch, as shown in Figure XI-3. Chemically

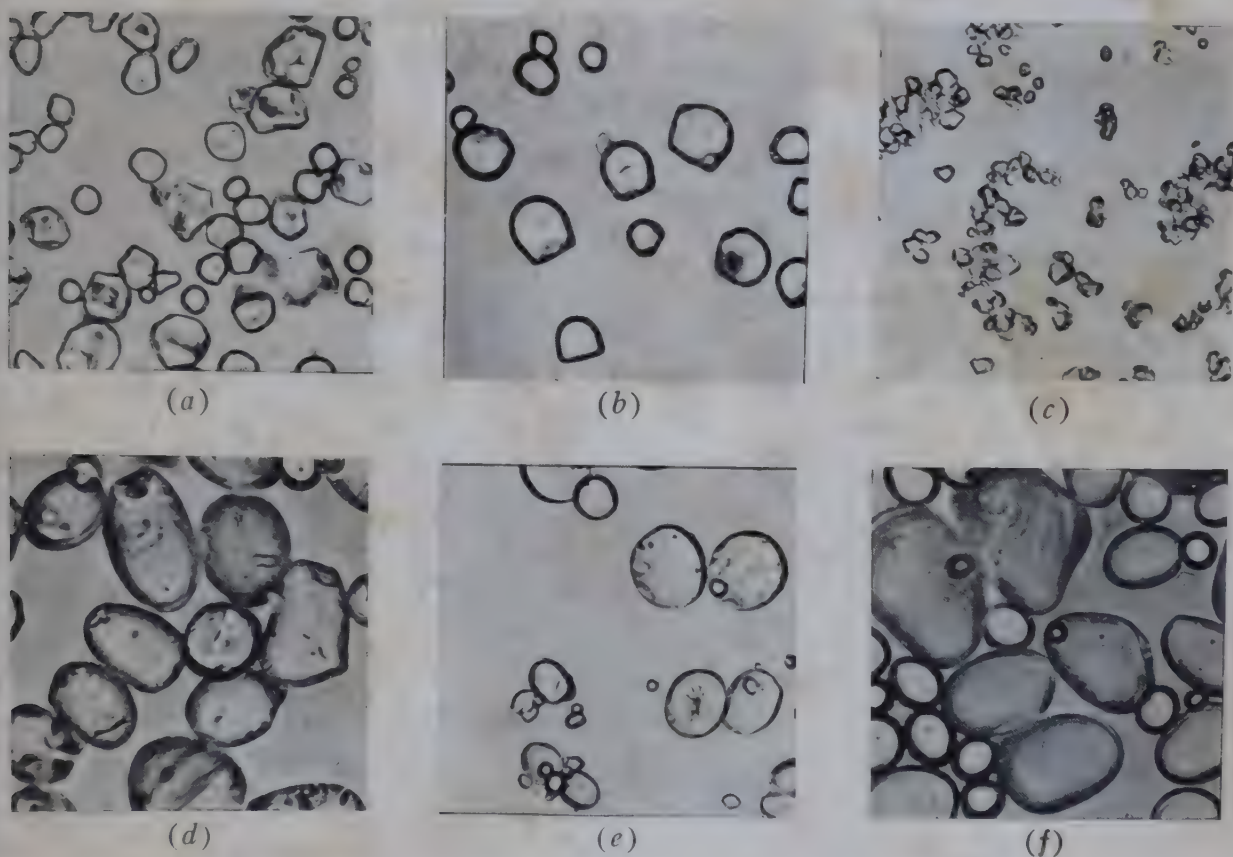


Fig. XI-3. Photomicrographs of uncooked starch granules (285 \times): (a) corn; (b) tapioca; (c) rice; (d) sago; (e) wheat; (f) potato.

speaking, starch contains two major chemical entities, amylose (a straight-chain polymer of glucose) and amylopectin (a branched-chain polymer of glucose), although certain starches (waxy varieties) contain only amylopectin. All starches contain minor amounts of fatty acids, other lipids, proteins, and inorganic salts. A typical analysis of unmodified corn starch is shown in Table III.

Before starch can be used for surface sizing, it must be heated in water to a temperature of about 190 to 210° F. and held there for approximately ten to twenty minutes. During heating, the granules take on water, swell, part of the granule dissolves, and the granule starts to disintegrate. The degree of granule disintegration and the viscosity of the starch solution depend upon the type of starch, degree of modification, time and temperature of heating, and amount of agitation. Starch solutions are reasonably stable, but there is some retrogradation upon aging in that the solution tends to cloud up, increase in viscosity, and even gel if the concentration is high enough. Retrogradation is increased by low pH, low temperature, presence of certain cations (e.g., calcium or aluminum), and slow cooling. The leaching of alum from the paper as it passes through the size is a factor in this connection.

Solutions of native or unmodified starch have too high a viscosity for ordinary surface sizing, and hence modified starches of lower viscosity are

TABLE III
TYPICAL ANALYSIS OF UNMODIFIED CORN STARCH

Color	White
Form	Pearl
Moisture, %	12.5-14.5
pH	4.5- 5.0
Acidity (to phenolphthalein)	0.055
Cold water soluble, %	0.32
Protein, %	0.3- 0.5
Ash, %	0.1
Ether extract, %	0.1- 0.2

generally used. The two types of modified starches most generally used are the oxidized starches and the enzyme-converted starches. Oxidized starch is the best all-around type for surface sizing, but enzyme-converted starch is also widely used in surface sizing and has proved satisfactory on all but the very highest grades of paper. A choice might be made between enzyme-converted starch and oxidized starch on the basis that oxidized starch works best on rag papers, whereas enzyme-converted starch produces acceptable results on chemical wood pulp and rag content papers. The enzyme-converted starches are considerably cheaper to use and naturally are preferred when there is no significant difference in results. Ordinarily, if there is any difference in results between these two types of starch, the difference shows up in the degree of sizing of the paper, rather than in the strength of the paper.

Oxidized starch is made by the starch manufacturer in a wide range of viscosities by treating a slurry of native starch with alkaline sodium hypochlorite at a temperature no higher than 130° F. During conversion,

soluble products are formed, and these are later removed by filtering and washing, after which the starch is dried and packed for shipment. Oxidized starches must be cooked in water at the paper mill by heating to a temperature of 190 to 210° F. for about fifteen to twenty minutes. Oxidized starch forms solutions of improved colloidal properties compared to most other forms of modified starch.

Enzyme-converted starch must be made at the paper mill by converting special starches manufactured for this purpose with enzyme. Enzymes are biocatalysts sold in liquid, powdered, pellet, and capsule form. The liquid preparations are less stable than the other forms and hence are not recommended when the product must be stored for a long period. All enzymes, whether liquid or dry, should be stored in a cool place. In converting starch with enzyme, the starch is made into a slurry with cold water at the desired concentration, and the pH of the slurry is adjusted between 6.5 to 7.5. The correct amount of enzyme (generally from 0.05–0.6%) is added, heat is applied, and from then on, a definite time-temperature schedule is followed. Different schedules may be used, depending upon the type of enzyme used and the concentration at which the starch is being converted. For dilute solutions such as ordinarily are used in surface sizing, the heating schedule can be controlled so that the temperature rises at a steady rate of about 2½° F. per minute up to the boiling point. Another method is to hold the mixture at the optimum temperature for enzyme activity (166–168° F. for corn starch) for twenty to thirty minutes, or until conversion is complete. Another method, which is more satisfactory when the concentration is very high, is to hold the mixture for a short period of time at 158 to 160° F. until the starch is partially reduced in viscosity and then heat to 166 to 168° F. for the remainder of the conversion period. At the end of the conversion period, the temperature should be raised to 200 to 210° F. and held there for ten to fifteen minutes to inactivate the enzyme and cook the starch. In some cases, chemicals (copper sulfate, formaldehyde, alkalies, etc.) may be used to inactivate the enzyme. Automatic equipment is available for controlling the enzyme conversion of starch.

In addition to the oxidized starches and enzyme-converted starches, special dextrans are sometimes used for surface sizing. These can be purchased in several different viscosities and can be cooked in the same manner as the oxidized starches. One of the newest corn starch products is a derivative consisting of the sodium salt of a low substituted starch acid ester containing carboxylic acid and sulfonic acid groups. This derivative can be cooked the same as the regular oxidized starches, but it has a lower gelatinization temperature. It produces very clear, water-white solutions

which are free from retrogradation tendencies. These derivatives are generally more expensive than the other types of modified starch.

Sizing with Starch in Size Press or Size Tub

The type of starch used in the size press or size tub varies all the way from solutions of unmodified (native) starch to solutions of oxidized or enzyme-converted starch of very low viscosity. As a general rule, modified starches of medium viscosity are used, although this depends upon the results desired.

As a rule, the higher the viscosity of the starch, the greater the improvement in the strength of the paper per unit of starch applied. On the other hand, the lower the viscosity of the starch, the greater the concentration at which the starch can be used and the greater the amount of starch added to the paper. High-viscosity solutions of unmodified, slightly oxidized, or lightly converted enzyme-converted starch are sometimes used where erasure and scuff resistance are most important, because such high-viscosity starch solutions tend to remain on the surface of the paper where they produce a tough, durable surface. However, when maximum sizing effects or maximum strength build-up are desired, it is better to use a modified starch of medium to low viscosity, since this type of starch penetrates farther into the paper where it tends to build up the internal strength and internal sizing, as well as produce a surface film. When sizing is the major effect desired, oxidized starch will generally give the best result. However, a properly prepared starch of either the oxidized or enzyme-converted type would be expected to result in an increase in sizing of approximately 30 to 50% (as measured by the ink flotation method) when applied at a concentration of about 10% solids. At the same time, a marked increase in burst, tensile, and fold should be obtained, although the tear is generally reduced. If, for the sake of convenience, starches for surface sizing are divided into high- and low-viscosity types, the concentrations at which each type would ordinarily be applied is as follows:

Starch	Concentration, % by weight	Baumé
High-viscosity	4-10	0.5-3.0
Low-viscosity	6-18	1.0-8.0

The temperature at which starch is applied at the size tub or size press varies from 125 to 150° F. About 3.5% starch on the weight of the paper is added in surface sizing in the case of offset papers.

The grades of paper customarily surface-sized with starch include bonds, ledgers, offset papers, bristols, and envelope papers. Direct process (diazotype) papers developed by the semi-wet process constitute a special class (see Chapter XIX). This grade of paper requires a fairly high

degree of water resistance, and hence the starch size used on this paper generally contains urea-formaldehyde resin to make the starch water-resistant. The starch (oxidized or enzyme-converted) is cooked in the regular manner, usually at a concentration of about 1 lb. of starch per gallon of size, and after cooling to a temperature of about 140° F., urea-formaldehyde resin is added in the form of a syrup. Approximately 10 to 20% resin, calculated as dry resin, is used on the basis of the starch. After the resin and starch are thoroughly mixed, papermaker's alum is added to bring the pH to about 5.0 to 5.5. During drying of the sized paper, the resin reacts with the starch to produce a water-resistant film on the surface of the paper. Full water resistance may be obtained soon after the paper leaves the driers, or one to two days' aging may be required in some cases to obtain maximum results. The water resistance developed depends upon the amount of resin used, the pH of the size solution, and the amount of heat applied to the paper after sizing.

A qualitative test for starch in paper is based upon the formation of a blue color when the paper is treated with iodine-potassium iodide solution. This test is very sensitive and produces a blue color when only very small amounts of starch are present. Some papers give a faint blue color in the absence of starch, due to the reaction between iodine and the non-starch constituents. Before carrying out the test, the paper (or water extract of the paper) should be acidified slightly before the iodine solution is added, since the blue color is fugitive under alkaline conditions.

A quantitative test for starch in paper is carried out by first treating the paper with salt-saliva solution to solubilize the starch. The filtered extract containing the solubilized starch (which should be free of any fibrous matter) is then digested in hydrochloric acid solution to hydrolyze the starch to dextrose. The hydrolyzed solution is next treated with Fehling's solution whereby the dextrose converts the copper into cuprous oxide. The amount of cuprous oxide is determined either gravimetrically or volumetrically. If the volumetric method is used, the cuprous oxide is first dissolved in molybdophosphate solution and then titrated with potassium permanganate. Factors are available for converting the results into grams of starch.

If no beater starch is present in the paper, it is possible to determine the depth of penetration of surface-applied starch by stripping back successive layers of the paper, using Scotch tape for removing each layer, and then staining the paper with iodine solution. By calipering the sheet at the beginning and after each layer is stripped off, it is possible to measure the depth of penetration. A binocular microscope aids in making this test.

Calender Sizing with Starch

Starch is widely used for the calender sizing of paperboard. In this process, starch solution is run in one or more boxes on the calender stack to increase the finish of the board and improve the printing properties. Some of the grades of board which are commonly calender-sized are boxboard, container board, manila, and patent coated board.

Because of the great interest which is being shown in high gloss inks for the printing of paperboard, many board mills use calender starch. When starch is properly applied, it is possible to reduce the penetration of printing ink and thereby improve the sharpness of the printing. If the board is printed in a box plant connected with the paper mill, the savings in ink are sometimes enough to pay for the cost of calender sizing.

Both high-viscosity and low-viscosity starches are used for calender sizing. Kraft papers are sometimes calender-sized with a solution of unmodified (native) starch of high viscosity in order to obtain maximum scuff resistance at minimum cost. However, on grades where printing qualities are of particular importance, highly modified starches are generally used at high concentrations, oftentimes as high as 12 to 24% solids, in order to apply a relatively large amount of starch to the board. At these high concentrations, it is sometimes necessary to add wax emulsions to the starch solution to prevent sticking on the calender rolls. The starch solution is usually applied at a temperature between 140 to 180° F.

In the calender sizing of cylinder machine board, the viscosity of the solution is determined by the type and character of the liner stock. If long, slow stock is used in the liners (e.g., in kraft or jute-lined board), a solution of relatively high viscosity can be used without trouble. However, if free stock is used in the liners (e.g., in white patent coated and bleached manila-lined board), the solution must have a relatively low viscosity in order to avoid pulling the liner loose and plugging the stack. The addition of wax emulsions or the use of special calender starches containing wax are desirable for the latter grades of board.

The number of boxes used for applying starch on the calenders depends upon the results desired. If both sides of the board are to be sized, two or more boxes are required. Usually one box for each side of the board is sufficient, although in some cases, two or three boxes may be used on one side. The greatest proportion of strength increase and fiber cementing is accomplished in the first box, but a second and third box is often desirable to obtain an even surface film for greater oil resistance. The boxes are generally located on the first calender stack near the top of the stack in order to allow sufficient time after treatment for drying of the sized board. In some mills, a water box is used ahead of the starch, but this tends to satisfy the absorptiveness of the board before the starch is added and thereby reduces the

amount of starch picked up in the second box. There is no advantage in running a water box after the starch box.

Surface Sizing with Animal Glue

Animal glue has been used as a surface-sizing agent for high-quality papers for many years and is still widely used on high-quality rag and rag content papers (e.g., banknote papers). Most of the glue used for surface sizing comes from the large American packing companies, although some glue comes from Argentina and Europe.

Animal glue is a protein which is derived from animal bones (ossein) or from animal skins, sinews, and tendons (collagen). The raw proteins are insoluble in water, but after treatment with acid and alkali, they become soluble in hot water (60° C. or above), due to conversion into glue or technical gelatin. In preparing glue from skins, the skins are first washed to remove dirt and are then soaked in lime water or given other forms of acid and alkali curing. This dissolves the more readily soluble substances (e.g., mucins, globulins, and albumins) and "cures" the glue protein. Next, the stock is washed, neutralized with acid, washed again, and extracted with hot water to remove the protein. Several extractions are made, but the highest quality glues are obtained from the first extraction. In making glue from bones, the bones are cooked under pressure with successive lots of water. Here again, the highest grades of glue are obtained in the first extraction. The glue solution is evaporated under vacuum at low temperature, and then the resulting solution is cooled to form a jelly which is dried by slow and careful air drying. The final product is then ground or flaked and packed for sale. Glue is tested and graded on the basis of routine tests which include viscosity, jelly strength, ash content, moisture content, pH, per cent grease, color, temperature of liquefaction, and temperature of gelation. The jelly strength, which is measured by means of a special gelometer, and the viscosity furnish useful information on the adhesive qualities of glue. The free grease content of the glue should not be more than 0.3% in order to avoid grease spots (fish eyes) on the paper, but a small amount of grease may be desirable in keeping down foam. The pH of glues generally varies from 5.5 to 7.5. Glues may be purchased with defoamer added.

Both hide and bone glues are used for surface sizing, but high-quality hide glue (or technical gelatin) is best for the higher grades of paper. Hide glues have a higher viscosity, gel more readily, set to stronger gels, produce more flexible films, and impart greater strength to paper than bone glues. Because of their better coverage and film-forming properties, high-grade hide glues often prove less expensive in the long run than the low-grade glues. Marked improvements have been made in the production of green

bone glue since World War II which has made this type of glue acceptable for uses where it had never been acceptable before.

To prepare glue for surface sizing, the dry glue in either granulated or flake form is soaked in cold water for about two hours. (Longer soaking is inadvisable in warm weather, unless a preservative is added.) After softening, the glue is heated, preferably by indirect heat, to about 140° F. and stirred gently until a uniform colloidal dispersion is obtained. Overheating should be guarded against to avoid hydrolysis and resultant decrease in viscosity and gel strength of the glue. The greatest percentage loss in strength from overheating occurs in the first few hours,²⁷ so that even a short period of overheating may be serious. Ordinarily, glue solutions are applied at a temperature between 90 and 130° F.

Alum is sometimes added to the glue solution. In small amounts, this causes thickening of the glue, but further addition results in a loss in viscosity. Hence, alum can be used to control the viscosity and also serves as a preservative. Alkalies are sometimes added to glue, but they tend to produce foam. Other causes of foam are mucin and peptones present in the glue itself. The pH should be around 6.0 to 6.5 for best results.

In some cases, glue is mixed with starch to reduce the cost of the size and also to make the broke easier to repulp. Glue and starch are incompatible and tend to separate unless the mixture is continually stirred. The addition of a small amount of soap (0.25 to 1.0% on the weight of the glue) is helpful in preventing separation.

Surface sizing with glue imparts to the paper a relatively hard, non-absorbent surface which improves the writing and erasing qualities of the paper. If the glue is hardened by passing the sized paper through a bath of alum or formaldehyde, the surface becomes quite resistant to water. Blueprint papers are customarily made in this way, since they must have a high wet tensile strength, but this is generally not done on glue-sized ledger bond.

Glue-sized papers are sometimes made by the wet soak process in which the glue-sized paper is reeled while still wet and allowed to stand until the glue soaks into the paper. When soaking is complete, the paper is dried on an air (Barber) drier. The final result is a very hard, durable paper which is a good imitation of high-grade, loft-dried paper.

Glue-sized papers should be dried under carefully controlled conditions since, in effect, drying consists of the removal of water from a gel-like layer on the surface of the paper. This means that the water should be evaporated at a temperature below the liquefaction point of the gel. Also, the water removal should be gradual and should not be carried beyond the point where checking of the glue film results. During drying, there is a

²⁷ O. V. Simonson, *Paper Trade J.* 115, No. 18: 227-228 (Oct. 29, 1942)

tendency for the glue film to shrink more in thickness than in length or width, because the film is firmly attached to the paper and cannot move freely in a lateral direction. If the film is rewetted with water, it tends to reassume the shape which it possessed at the time of gel formation, and consequently it tends to swell chiefly in thickness. As a rule, glue films absorb water slowly, and for a case-hardened film, it may take as long as twelve weeks' exposure to reach equilibrium.²⁸ Glue-sized papers are sometimes plasticized with hygroscopic salts, glycerine, or sulfonated oils to increase the pliability of the surface film and to reduce checking in an atmosphere of low humidity.

A qualitative test for nitrogen (casein, glue, etc.) in paper can be made by boiling the paper in 1% caustic soda solution, neutralizing the filtered extract, and treating with Schmidt's reagent (ammonium molybdate and dilute nitric acid). A white precipitate indicates the presence of nitrogenous material. Sometimes tannic acid is used as a precipitant in place of Schmidt's reagent, but this test is not reliable in the presence of starch.

A quantitative test for nitrogen in paper can be made by the well-known Kjeldahl determination. This test indicates the quantity of nitrogenous sizing agent (such as glue, soybean protein, and casein) in the paper, but includes other ammoniacal nitrogen derived from materials such as urea and melamine formaldehyde resins. The Kjeldahl determination is carried out by digesting the paper in a mixture of sodium sulfate and sulfuric acid containing a selenium compound and mercury until the mixture becomes colorless. The mixture is then neutralized and an excess of sodium hydroxide is added. Distillation is then carried out with the delivery tube of the condenser beneath the surface of a measured amount of 0.1 *N* acid. The contents of the flask are distilled for about forty-five to sixty minutes, after which the contents of the receiver flask are titrated with 0.1 *N* sodium hydroxide. The per cent nitrogen can be determined by the following relationship:

$$\frac{\text{ml. of base} \times \text{normality of base} \times 0.014 \times 100}{\text{weight of sample}}$$

A blank determination on the reagents should always be made. The amount of specific nitrogenous material can be determined by multiplying the per cent nitrogen by a suitable factor. The factors are listed below:

Glue	5.6
Casein	6.3
Urea-formaldehyde resin, i.e., Uformite 467	4.13
Urea-formaldehyde resin, i.e., Uformite 470	3.41
Melamine resin, i.e., Parex 607	2.6

²⁸ C. M. Mason and H. E. Silcox, *Ind. Eng. Chem.*, 35, No. 6: 726-729 (June, 1943)

Surface Sizing with Other Materials

A number of water-dispersible materials possessing good film-forming characteristics have appeared on the market within fairly recent years, among the best known of which are carboxymethylcellulose, methylcellulose, polyvinyl alcohol, and alginate. These materials make excellent surface-sizing agents, although their cost is relatively high compared with other sizing agents. They can be applied on the paper machine either at the size press or size tub and are widely used as a calender size for paperboard to be printed with gloss inks.

Because of their relatively high cost, these materials should be used on dense papers and should be applied in as viscous a solution as possible in order to minimize excessive penetration into the paper. The viscosity of these materials is generally higher than glue and starch, and consequently they can be used as lower concentrations, which helps to reduce the consumption.

Use of Carboxymethylcellulose

One of the most promising of the newer surface sizing agents is carboxymethylcellulose. This material, which can be prepared by reacting monochloroacetic acid with alkali cellulose, is available in two principal forms, as the soluble sodium salt and as the soluble ammonium salt. The sodium salt of the type generally used for surface sizing has a degree of substitution of approximately 0.75.^{29,30} It forms clear solutions at a pH of about 8.0 and produces flexible, tough films. It can be dispersed by adding the dry powder to water slowly at a temperature of 60 to 70° C. under vigorous agitation. The solution can be used alone or mixed with starch, vegetable gums, or casein. Urea-formaldehyde resins can be added to improve the water resistance.

A comparison of the results obtained in calender sizing with carboxymethylcellulose and with starch are shown in Table IV. These results were obtained in an extended mill test on white patent coated board for gloss ink printing. In both cases, the solutions were applied to the top liner of the board in a single box located on the fourth roll from the top of a six-roll calender stack. It can be seen that a 1% solution of carboxymethylcellulose produced results comparable to a 12% starch solution, so far as oil absorption is concerned. The strength obtained with the carboxymethylcellulose was, however, slightly lower than that obtained with starch.

Horsey²⁹ has described results obtained by the surface application of a low-viscosity carboxymethylcellulose to paper and paperboard at the size

²⁹ E. F. Horsey, *Tech. Assoc. Papers* 30: 294-298 (June, 1947)

³⁰ C. J. Brown and A. A. Houghton, *J. Soc. Chem. Ind.* 60: 254-258 (1941)

press and calender stacks. She has found that the application of a 4% solution at the calenders (0.3 lb. of carboxymethylcellulose per ream) gave a higher oil resistance than necessary for optimum printing with gloss inks (see Figure XI-1). The treated boards had relatively little resistance to thin vehicles (turpentine), but had a marked resistance to heavy oils and printing inks. When carboxymethylcellulose was applied to offset paper at the size press (0.5 lb. per ream), the Dennison wax pick test was increased from a No. 9 to a No. 18 wax.

The amount of carboxymethylcellulose in paper can be determined quantitatively by extracting the paper with sodium hydroxide, treating the extract with sulfuric acid to produce glycolic acid, and measuring the amount of glycolic acid colorimetrically.³¹

TABLE IV

COMPARISON OF SPECIAL CALENDER STARCH AND CARBOXYMETHYLCELLULOSE FOR CALENDER SIZING

Type of material used	Concentration of size, %	Dennison wax pick	Oil absorption ^a
Carboxymethylcellulose	1	12	30
Special converted corn starch ...	12	13.5	30
Water alone in box	0	9	9

^a Time in seconds for complete absorption of a thin film of oil.

Use of Methylcellulose

Methylcellulose is a useful water-dispersible sizing agent which has some use for surface sizing. The commercial water-soluble grades of methylcellulose, which normally contain between 1.7 to 1.9 methoxyl groups per glucose unit, are available in a range of viscosity from 10 cps. to 4,000 cps.

To prepare a solution of methylcellulose, the dry product should be mixed in hot water, and then when the mass is thoroughly wetted, it should be cooled and stirred until a clear solution is obtained. Heating of methylcellulose solutions decreases the viscosity at first, but then increases the viscosity until a critical temperature is reached, at which point the solution is transformed into a gel, or the methylcellulose is precipitated if the solution is very dilute. The temperature of gelation depends upon the concentration and viscosity of the methylcellulose solution, solutions of high concentration tending to gel at the lower temperatures. Cooling of a gelled solution brings it back to its original state.

Methylcellulose can be used by itself for sizing, or it can be used in combination with starch or animal glue. Recently, modified methylcellu-

³¹ R. W. Eyler and R. T. Hall, *Paper Trade J.* 125, No. 15: 165-168 (Oct. 9, 1947)

loses (Methocel HG) have been made available which have increased solubility in warm water, and these derivatives are particularly useful for modifying starch sizing formulations. Solutions of methylcellulose are relatively stable and ordinarily require no preservative. They are not appreciably affected by pH over a range of 2 to 12, although alkalis tend to increase the viscosity. Certain anions (NO_3 , Cl, and SO_4) exert a coagulating effect, and others (SCN and I) exert a dispersing effect.

Methylcellulose produces hard, flexible, continuous films which are impervious to oils and greases. The film is water-sensitive, although it is possible to improve the water resistance by incorporating 5 to 20% of water-soluble urea formaldehyde resin in the methylcellulose solution. Plasticizers (e.g., glycerol, invert sugar, or sorbitol) are sometimes used to improve the flexibility of the film.

Methylcellulose is used principally for sizing against grease and oils and has proved effective for making oil-resistant papers and paperboards. It is used for the surface sizing of waxing and carbonizing papers where the film of methylcellulose is effective in reducing porosity and for improving the hold-out of the waxy surface treating materials. For paperboards to be printed by gloss inks, the application at the calenders of 0.03 to 0.20 lb. of methylcellulose per 1,000 sq.ft. of paper surface will produce a marked improvement in the gloss of the ink.³² Methylcellulose can be readily applied by size press or coating machine, but in calender sizing, where temperatures of the size often reach 175° F., it is necessary to circulate and cool the solution in order to prevent coagulation of the methylcellulose with resultant picking of the stock. For this application, the specially modified methylcellulose already mentioned (Methocel HG) is most suitable, since it provides a working margin of 10 to 20° F. over regular methylcellulose.³³

Use of Polyvinyl Alcohol

Polyvinyl alcohol is a water-soluble member of the class of vinyl resins which is made from vinyl acetate by hydrolysis. The solubility and film-forming characteristics of polyvinyl alcohol vary according to the degree of replacement of acetate groups with hydroxyl groups. The range runs from the completely hydrolyzed product (less than 1% acetate groups), which disperses readily in water and produces films of very high tensile strength, to the partially hydrolyzed products which are insoluble in water. Some of the intermediate products require heating to 60 to 85° C. to obtain solution in water. The range of viscosity of commercial polyvinyl alcohols is

³² R. M. Upright and F. C. Peterson, *Paper Trade J.* 110, No. 18: 245-249 (May 2, 1940)

³³ Article by Dow Chemical Co., *Paper Mill News* 73, No. 20: 78 (May 20, 1950)

very great, being greater than that obtainable with the water-soluble cellulose derivatives.

Polyvinyl alcohol forms films which have a very high tensile strength and a very high degree of transparency, flexibility, and oil resistance. The water resistance is rather poor, but this can be improved by treatment with urea formaldehyde resins or with chromic compounds (chromic acetate, cupric dichromate, or sodium dichromate).

Solutions of polyvinyl alcohol can be applied at the size press or at the calenders. The high- or medium-viscosity grades are generally used in calender sizing, usually at a concentration of 1 to 3%. The printing qualities of the board are noticeably improved by applying as little as 1 lb. of polyvinyl alcohol for each 15,000 sq.ft. of paperboard. A double application involving polyvinyl alcohol, a starch-polyvinyl alcohol mixture, or straight starch in the first application, followed by straight polyvinyl alcohol in the second application, is even more effective.

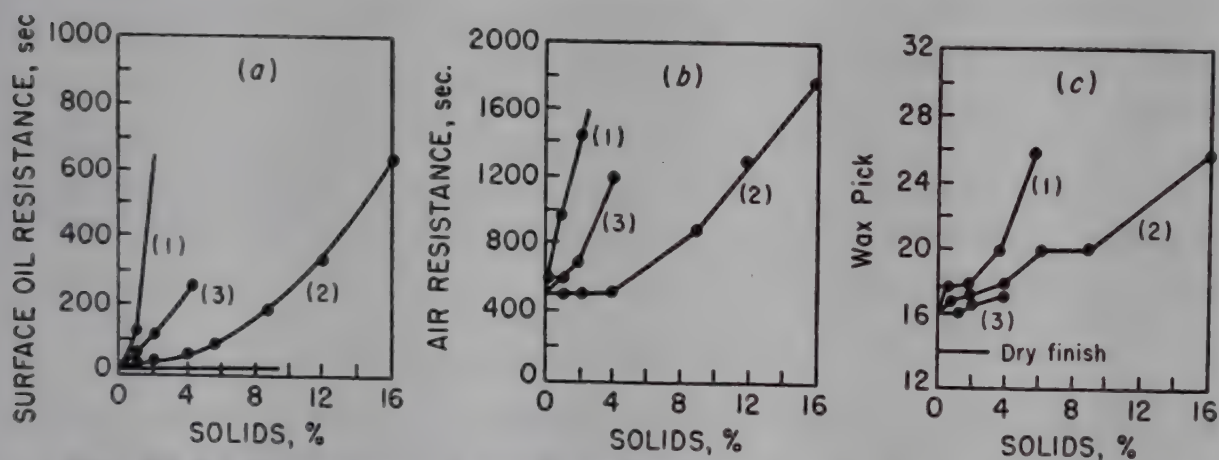


Fig. XI-4. Comparison of starch and polyvinyl alcohol in calender sizing for effect on (a) surface oil resistance, (b) air resistance and (c) wax pick: (1) polyvinyl alcohol; (2) oxidized starch; (3) tapioca starch.

A comparison of oxidized corn starch, tapioca starch, and polyvinyl alcohol for their effects on wax pick, surface oil resistance, and air resistance in the calender sizing of patent coated board was made by Yraola.³⁴ As can be seen from his results shown in Figure XI-4a-4c, polyvinyl alcohol is much more effective than starch in increasing the surface oil resistance and air resistance, but not much more effective than starch in increasing the wax pick test.

Use of Alginate

Algin or alginic acid is a high molecular weight carbohydrate polymer of anhydro- β -D-mannuronic acid which is obtained from a certain type of seaweed growing in quantity off the west coast of the United States. Al-

³⁴ A. Yraola, *Paper Trade J.* 116, No. 21: 231-232 (May 27, 1943)

ginic acid is insoluble in water, but it contains a high percentage of carboxyl groups which can be reacted with alkali to produce soluble salts known as alginates. Some of the important commercial derivatives of alginic acid are those of potassium, propylene glycol, ammonium, and sodium, of which the last two are the most important industrially.

Alginates can be dissolved readily in water by adding the dry product to water under vigorous agitation. The solutions obtained are generally quite viscous, although alginates are available in high-, medium-, and low-viscosity grades. Heating tends to reduce the viscosity of the solution about 15% for each 10° F. rise in temperature.³⁵ Holding at high temperatures for long periods results in a permanent loss of viscosity, due to depolymerization. Solutions of alginates are thickened by acids at a pH of about 4.5 and precipitated from solution at a pH of about 3.0. Gel formation takes place at pH values over 12 and in the presence of heavy metal salts.

Alginates can be used for surface sizing alone or in combination with starch, casein, vegetable gums, or similar materials. Films produced by alginates are clear and tough, but are brittle unless plasticized, and are water sensitive unless treated with urea-formaldehyde resins or precipitating salts. Because of their high viscosity and their tendency to remain on the surface of paper, alginates are effective as surface-sizing agents even when used at concentrations as low as 0.4 to 2.0%.

Use of Wax Emulsions

Most of the materials used for surface sizing belong to the class of water-dispersible colloids. At times, it is desirable to add water-insoluble materials, such as waxes or resins, in a surface-sizing operation, and emulsions offer one of the best means of doing so. To be effective, the particles of resinous or waxy material should be in a fine state of subdivision so that the effects obtained are comparable to those obtained with water-dispersible colloidal materials.

There are two principal types of wax emulsions, namely, the soap type and the acid-stable type. The soap type emulsions are sensitive to acids and heavy metal salts. They do not penetrate paper readily, because the residual salts and acids in the paper generally cause immediate precipitation of the wax near the surface of the paper.³⁶ However, this type of emulsion is likely to coagulate in the size tub or calender box, on account of acid or alum leached from the paper. Acid-stable emulsions are much more resistant to the coagulating effects of salts and acids, and hence are preferred over the soap type emulsions for most surface-sizing applications. They

³⁵ "Algin at Work," Kelco Co., Chicago, Ill. (1940)

³⁶ R. W. Kumler, *Paper Trade J.* 104, No. 10: 36-38 (Mar. 11, 1937)

have low wetting ability which is advantageous, since this reduces the penetration of emulsion into the paper, thus reducing the cost and preventing the formation of overly wet paper. The characteristics of several commercial wax emulsions are shown in Table V.³⁷

Wax emulsions can be used at the size tub or size press in combination with starch, or they may be used in calender sizing, either alone or in combination with starch. Surface sizing with wax emulsions imparts a number of desirable properties to the paper, such as improved finish, in-

TABLE V
CHARACTERISTICS OF WAX EMULSIONS

Recommended use for emulsion:	A	B	C	D
	Beater and surface sizing	Beater and surface sizing	Beater and surface sizing	Surface sizing
Solids content, %	41	46	46	46
Type of solids	Paraffin wax	Paraffin wax	Microcrys- talline wax	Blend of paraffin and micro- crystalline wax
Pounds per gallon	8.0	8.0	8.0	8.0
Melting point of wax, °F. (AMP)	125	125	155	143
Particle size, microns (1/25,000 in.)	1.3	1.3	1.3	1.3
Properties of commercial emul- sion diluted with 9 parts of water:				
Surface tension, dynes/cm.	70	39	39	35
Resistance to alum, %	Unlimited	0.09	0.09	0.20
Resistance to hard water, p.p.m.	Over 2000	200	200	200

creased resistance to scuffing, and increased water repellency and water resistance. In calender sizing, the wax serves the additional function of a lubricant for preventing the starch from picking the surface of the paper-board. The increase in water resistance obtained from wax emulsions is not due to the formation of a continuous film of wax, but to the coating of the fibers with microscopic particles of wax which increase the contact angle of the fibers with water.³⁸ These wax particles also decrease the amount of loose surface fiber or "fuzz," thus improving the printing properties and the scuff resistance.

When surface sizing with wax, it is desirable to keep the wax on the surface of the paper. This is not a problem when materials such as starch

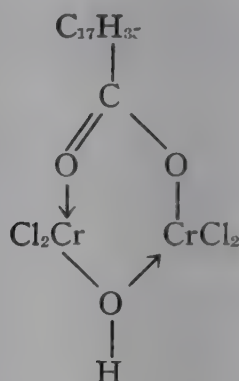
³⁷ Emulsions made by Socony-Vacuum Oil Co., Inc.

³⁸ J. C. Dean, *Paper Mill News*, Superintendents' Number, 74-78 (June 16, 1945)

are used with the wax, since the starch tends to hold the wax on the surface, but excessive penetration may result when wax emulsions are used by themselves. Paper surface-sized with wax should be stored at temperatures below the melting point of the wax to keep the wax from melting and penetrating farther into the paper. Too much wax should not be applied in surface sizing since this acts as a lubricant and may cause trouble in winding of the paper and in slipping of paper off the skids.

Sizing with Stearato Chromic Chloride Complex

A comparatively new product for imparting water repellency and sizing to paper is stearato chromic chloride,³⁹ a Werner type chromium-stearate complex with the following formula:



This material is sold as a dark green liquid containing 30% of the complex in an isopropyl-water mixture composed of 60% alcohol and 10% water. The commercial solution is diluted with water to about 1 to 7% (commercial basis) and applied to the paper at the size press, size tub, or calender stacks at a temperature of 80 to 100° F. and a pH of about 3.2

Water repellency is obtained as a result of the chromium atoms anchoring to the negatively charged fibers, leaving the stearate groups projecting outward to form a water-repellent surface. Heating of the treated paper to 200° F. or higher is necessary to obtain maximum results, and under proper conditions, excellent water repellency can be obtained with a retention of about 0.6 lb. of commercial material per 10,000 sq.ft. of paper surface. The strength of the paper is not appreciably altered, although the brightness of white papers is reduced by about 1 to 2 points.

Other Surface Applications

Many miscellaneous materials are sometimes applied in a size press or size tub. These materials are not sizing agents, but since they are applied in the same manner as sizing agents, a few of them are mentioned below.

Viscose has been suggested for surface application to paper, although it

³⁹ Sold under trade name of Quilon by Grasselli Chemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

is not used commercially to any extent. Richter⁴¹ has patented a process by which a waterleaf sheet is passed through a 1 to 5% solution of viscose. Cellulose is subsequently regenerated on the surface of the paper by treating the paper with heat or an acidic material.

Paper is sometimes treated with fire retardants. The materials used for this purpose are usually ammonium salts, such as ammonium phosphate, ammonium sulfamate, or ammonium sulfate. The materials are dissolved in water and applied either at the size press or at the calenders or, in some cases, by addition at the beater.

Certain grades of paper are treated with plasticizers to produce a softer sheet. This is not a sizing operation, although plasticizer is sometimes added to sized papers to overcome the stiffness imparted to the paper by the sizing agent. Glycerine, sorbitol, mannitol, and glycols such as diethylene glycol, dipropylene glycol, and polyethylene glycol are among the softeners used. These materials are usually applied in water solution at the size press on the paper machine or in a separate operation on a dampening machine. In some cases, they may be applied at the calenders. Glassine, parchment, and waxing stock are some of the grades commonly treated with plasticizer. Glassine is usually treated with a 10% solution of glycerine or a mixture of 5% glycerine and 5% corn syrup. The solution is applied by means of a dampening or kiss roll, although in some cases, a regulation size tub or size press may be used. The former method gives less uniform distribution and makes it necessary that the paper be conditioned in roll form before supercalendering in order to permit uniform absorption of the plasticizer. The paper will pick up the plasticizer best if it is slightly damp.

Coating with Water-Soluble Materials

Coating of paper with water-soluble materials is closely related to surface sizing. A distinction can be made, however, on the basis of the method of application and the amount of sizing material applied. Surface sizing is carried out on the paper machine, and the amount of sizing agent applied is usually quite small. In contrast, coating is generally carried out in a separate operation, and the amount of material applied is much greater.

Roll, brush, spray or, in fact, almost any type of coating machine can be used for applying the coating. The coating solution is usually applied at high solids content in order to obtain a heavy layer of coating on the surface of the paper. It is quite common to apply the coating in two stages, and sometimes to apply different coating materials in the separate stages. For example, a coating of starch may be applied in the first stage and a

⁴¹ G. A. Richter, U. S. 2,018,875 (Oct. 29, 1935)

coating of polyvinyl alcohol applied in a second stage. These types of coating are used primarily for grease-resistant papers.

Use of Starch

Starch produces a coating of relatively poor oil resistance because of its brittle film, although it is fairly effective if the paper is not creased. The flexibility of starch coatings can be improved by mixing with better film-forming substances such as polyvinyl alcohol or methylcellulose, although starch is not truly compatible with these materials. Plasticizers are helpful, but well-plasticized starch films are likely to become sticky at high humidities, and lightly plasticized films are too brittle at low humidities.

Starch is sometimes used as the first coating in double coating processes. The starch fills in the pores of the paper and furnishes a smoother and more receptive surface for the final coating.

Starch is used in the manufacture of decalcomania or transfer papers. In making these papers, a heavy film of starch is applied to the felt side of the paper as an undercoating, and then the printing is applied over this. A lacquer coating may be applied over the starch to improve the ink receptivity. Later, when water is applied to the back of the sheet in the transfer process, the starch film dissolves and releases the printed matter. The base stock is generally a sulfite stock, preferably of high wet strength. The starch is usually applied by brush coating.

Use of Proteins

Greaseproof papers are sometimes made by coating paper with thick films of plasticized animal glue or casein. A typical formula is given below:⁴²

Glue	11.1%
Glycerine	13.3%
Cane sugar	3.1%
Anti-foam	0.9%
Water	71.6%

Zein has also been used for the same purpose. Usually, however, this protein is dissolved in alcohol, rather than in water, so that the coating is more appropriately classified as a varnish.

Use of Sodium Silicate

Sodium silicate is sometimes used as a surface coating for paperboard. Silicate-coated board is used for the packaging of coffee, chocolate, cookies, candy, crackers, and spices to prevent the loss of fragrant oils and to pre-

⁴² H. Bennett, *Chemical Formulary*, Vol. 7, p. 327. Chemical Publishing Company, New York (1945)

vent oil and grease from staining the carton. The stiffness of paperboard is increased by coating with silicate, and the paper is made slightly fire-resistant. Where moisture resistance is needed paraffin coatings can be applied over the silicated surface.

Low-viscosity solutions of silicate are generally used for coating, although concentrated solutions of high viscosity may be used where a thick surface film is desired. A suitable solution can be made by diluting 300 to 400 parts of silicate with 100 parts by volume of water. The most siliceous grades are recommended for coating because they dry faster, produce films of higher moisture and grease resistance, and cause less staining of the paper than silicates of low silica content. The 35° Baumé, 3.7 ratio silicate gives best results, although the 3.3 ratio grade is sometimes used.

Silicate may be applied to paper by dipping or roll coating. In commercial work, the amount of coating ranges from 2 lb. per 1,000 sq.ft. for papers to be overcoated with paraffin to 20 lb. per 1,000 sq.ft. for papers requiring a high degree of grease resistance.⁴³ An average coating for paperboard to be used in cracker boxes is 6 to 8 lb. per 1,000 sq.ft.

Silicate coatings tend to be brittle, particularly if applied in heavy films and consequently are sometimes treated with plasticizers such as glycerine, corn syrup, or rubber latex to increase the flexibility. The addition of oxidizing agents to silicate solutions (hydrogen peroxide) tends to inhibit staining of the board.⁴³ Silicate films tend to whiten and lose their gloss upon aging, due to absorption of carbon dioxide from the air, particularly if subjected to high concentrations of carbon dioxide before the film is dry.

Use of Polyvinyl Alcohol and Water-Soluble Cellulose Derivatives

Polyvinyl alcohol and water-soluble cellulose derivatives are used for coating where a high degree of oil resistance is desired. These materials are among the most effective agents known for this purpose. In order to reduce the cost of coating with these materials, the paper to which they are applied should be as dense and highly calendered as possible, and the solution should be applied in as concentrated and viscous form as possible, since this reduces absorption of sizing agent by the paper. If porous papers must be used, a presizing or precoating with some cheaper material such as starch is advisable.

The concentration of polyvinyl alcohol used for coating paper depends upon the type of equipment, grade of paper, and viscosity of the polyvinyl alcohol used. A cold 10% solution of high-viscosity polyvinyl alcohol can be applied by doctor knife. A hot 8 to 10% solution of medium-viscosity

⁴³ R. C. Merrill, *Tappi* 32, No. 11: 520-528 (Nov., 1949)

polyvinyl alcohol can be applied by brush or roll coater.⁴⁴ Using hot, low-viscosity coatings reduces the foaming tendency. Anti-foaming agents, extenders (starch, casein, etc.), or plasticizers may also be added. A suggested formula⁴⁵ is 10 parts polyvinyl alcohol, 5 parts glycerine, and 85 parts water.

⁴⁴ Vinyl Products Bulletin V-9-748, "Elvanol Polyvinyl Alcohol for High Gloss Printing and Greaseproof and Grease-Resistant Papers," Electrochemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

⁴⁵ Vinyl Products Bulletin V-9-748, "Elvanol Polyvinyl Alcohol for High Gloss Printing and Greaseproof and Grease-Resistant Papers," Electrochemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

WET STRENGTH

The property of wet strength is entirely different from that of sizing. Sizing refers to the rate at which water penetrates paper and has no relationship to the wet strength of the paper, since once water has penetrated into ordinary sized papers, the mechanical strength of the paper becomes practically non-existent. Thus, the wet strength of a rosin- or a wax-sized paper is not appreciably greater than that of an unsized paper, the only difference being that the sized paper takes longer to arrive at a condition where the sheet is saturated with water. In practice, it is possible to size paper to such an extent that there is practically no water penetration, and consequently it retains most of its original dry strength. Under these circumstances, sizing agents such as rosin keep water from coming into contact with the fibers in the interior of the paper. However, this is not a true wet-strength condition.

A number of factors affect the wet strength of paper. Increased beating increases wet strength, but the effect is only slight. Excessive drying of the papers results in a slight increase in the wet strength.¹ Increasing the ream weight increases the wet strength slightly, although this cannot be considered as a true wet-strength effect. Brecht² found that the percentage wet strength is the same for all thicknesses of a given paper when plotted against the percentage of water in the sheet. Generally, increased fiber length results in increased wet strength, although Brecht³ reports that a mixture of long and short fibers in groundwood papers produces a higher initial wet strength (before drying) than papers made from either the long or the short fibers alone.

Description of Wet-Strength Property

All papers retain a proportion of their strength, even when thoroughly saturated with water, but the strength retention is very small unless the paper has been given a special wet-strength treatment. Britt⁴ defines a

¹ W. S. Wilson, *Paper Trade J.* 128, No. 5: 40-44 (Feb. 3, 1949)

² W. Brecht, *Svensk Papperstidn.* 50, No. 11: 63-71 (June 15, 1947) through T. T. Collins and A. Adrian, *Paper Mill News* 72, No. 23: 10, 12 (June 4, 1949)

³ W. Brecht, private conversation at New York State College of Forestry (Apr., 1950)

⁴ K. W. Britt, *Paper Ind.* 26, No. 1: 37-44 (Apr., 1944)

wet-strength paper as one which retains at least 15% of its dry tensile strength when thoroughly saturated with water. However, it is not necessary for paper to be thoroughly saturated with water in order for the wet-strength property to manifest itself, since the strength of paper exposed to a moist atmosphere (so that the paper contains only 15 to 20% moisture) is dependent upon the amount of its wet strength.^{5,6} This is shown in Figure XII-1 where the tensile strength is plotted against moisture content for a wet-strength paper and an untreated paper made from the same stock.⁶

As pointed out previously, a high degree of rosin sizing will, in many instances, serve the same practical purpose as a true wet strength, but it should be recognized that there are fundamental differences between wet-strength papers and highly sized papers. True wet strength is produced upon the development of water-resistant bonds or bridges between adjacent

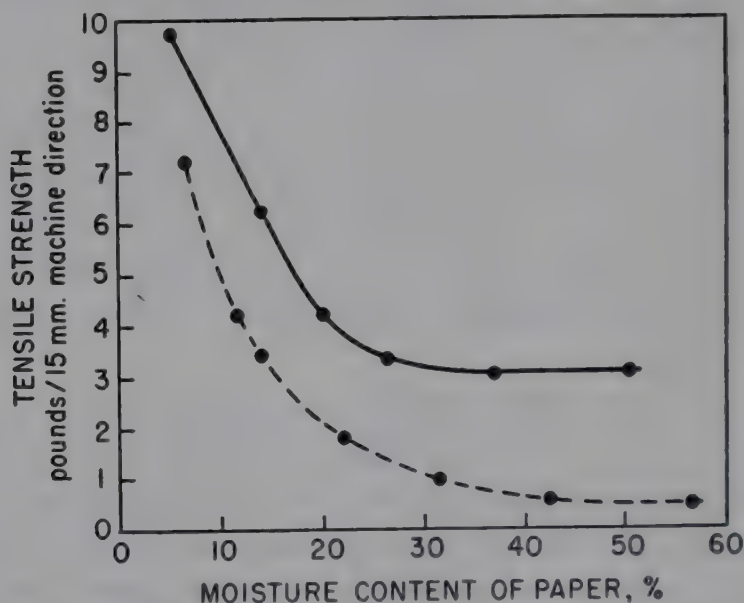


Fig. XII-1. Effect of moisture content on tensile strength of a wet-strength (—) and a non-wet-strength (untreated) (--) paper.

fibers in the paper. Ordinary paper has no appreciable wet strength, because the bonds formed between the hydroxyl groups of adjacent fibers are readily broken by water, due to a weakening of the secondary valence forces. Water also causes a reduction in the frictional forces due to a lubricating effect. If part of these bonds is replaced by water-resisting bridges (such as methylene bridges) which are formed when paper is treated with urea-formaldehyde or melamine-formaldehyde resins, a high degree of wet strength is developed. The treatment of fibers with periodate increases the wet strength to some extent because of the production of carbonyl groups which act as cross linkages between adjacent fibers.⁷

⁵ *Paper Ind.* 29, No. 7: 1006 (Oct., 1947)

⁶ K. W. Britt, *Tech. Assoc. Papers* 31: 594-596 (1948)

⁷ M. O. Schur and R. M. Levy, *Paper Trade J.* 124, No. 20: 221-224 (May 15, 1947)

Wet-strength resins increase the bonding between fibers, but do not appreciably change the strength of the individual fibers. This is indicated by the fact that the "zero span" tensile test is not changed.⁸ The theoretical upper limit of wet-strength papers in a wet condition is the wet strength of the individual fibers, assuming that the wet bond between the fibers is strong enough to resist any pull. From a theoretical standpoint, the wet strength of treated papers could be greater than the dry strength of the untreated paper if the wet-strength agent were effective enough. Commercially, however, the wet strength of treated paper is always far below the dry strength of the untreated paper.

Wet strength is a highly useful property in bag, tag, toweling, tissue, blueprint papers, map papers, paper draperies, paper patterns, frozen food wrap, and many other grades of paper. Wet-strength papers have potential value in such grades as coating base stock, lithographic printing papers, and impregnating and saturating papers or, in fact, any paper where freedom from linting and high strength are required in the presence of high moisture content. Within recent times, there has been a marked increase in the production of wet-strength papers, owing to the development of improved processes for making these papers. The importance of wet strength at the wet end of the paper machine is a consideration which, so far, has not been studied to any extent.

Measurement of Wet Strength

If a wet sheet of paper is allowed to return to its original dry condition without disturbing the fibers, it will recover practically all its original dry strength. Therefore, the only way in which the wet-strength property can be determined is by testing the paper for mechanical strength in the presence of water. There are several methods of testing the wet strength of paper, but the most common is the wet tensile strength.

Wet tensile strength is usually measured after the paper has been thoroughly saturated with water. Complete saturation is defined as exposure to water until the paper is wetted throughout and no appreciable loss in strength occurs on further soaking. Wet strength cannot be measured on papers impervious to water. In some cases, the wet strength is measured after the sample has been soaking in water for a stated length of time corresponding to the normal use conditions for that grade of paper. This measures sizing plus wet strength. The time of soaking may vary from several hours for heavy papers and paperboards to a few minutes for thin tissue papers. Wet bursting strength is sometimes used as a measure of wet strength and, in general, higher wet strength values are obtained by this method than by the tensile test.⁹ Wet tear is infrequently used. According

⁸ "For Instance." American Cyanamid Co., No. 32 (1947)

⁹ T. T. Collins and A. Adrian, *Paper Mill News* 72, No. 23: 10, 12 (June 4, 1949)

to Morgan,¹⁰ the wet tear of wet-strength paper is higher in some cases than the dry tear.

Wet tensile strength can be measured in a regular tensile tester without any attachments, if the paper can withstand handling when wet. For those papers which are difficult to handle when wet, a special attachment called the Finch wet-strength attachment can be used. This device consists of a stirrup made of two metal straps supporting a horizontal rod under which the test specimen is looped. A small movable container for holding water is located between the straps. In carrying out the test, the specimen is looped under the horizontal rod and both ends of the specimen are clamped in the upper jaw of the tensile tester. The container filled with water is then moved into place, immersing the specimen in water to a depth of 0.75 in. A regular tensile measurement is then made at the end of the proper immersion period. The indicated strength is divided by two to obtain the wet strength of a single strip.

As a rule, wet tensile strength is reported as the percentage of the dry tensile strength which is retained on complete wetting of the paper. This method of reporting eliminates the effect of basis weight, but it has obvious disadvantages, one of which is that papers of low absolute wet strength often show fairly high relative wet strength in comparison with the dry strength. Another way of expressing the results is by comparing the percentage wet to dry strength for the treated paper with the percentage wet to dry strength for the untreated paper, but this method also has the above disadvantages. Comparing wet strength to dry strength gives unexpected results in cases where different methods of treatment result in the same wet strength but different dry strengths. As was pointed out by Steenberg,¹¹ measuring wet strength as a function of dry tensile strength is not fair to the wet-strength paper, since the paper has a much greater utility than indicated by this sort of comparison. A more satisfactory measure of wet strength is the area of work under the stress-strain curve of the paper when force is plotted versus elongation of the paper. This method is not widely used, but it has the advantage of putting more emphasis on the toughness of the paper than on the tensile strength which, after all, is a better criterion of the serviceability of the paper. When tested in this way wet strength papers are found to have equivalent strength in the wet and dry states.

Another method of measuring wet strength is by means of the wet break test, which has already been described in the chapter on Internal Sizing. This test differs from the regular wet tensile test in that tension is applied during the entire soaking period. Thus, this test measures a combination of the sizing property and the wet-strength property and, as

¹⁰ J. D. Morgan, *Paper-Maker* 112, Annual Number 15: 17-18 (1946)

¹¹ Private communication with the author

such, is not a fundamental test, but it has great value as a use test. The wet break test indicates, for example, how well and how long a loaded paper will stand up when it is in contact with water. In contrast, the wet tensile test shows how well the paper will stand loading after it is thoroughly saturated with water.

Another means of measuring wet strength is by rubbing the water-saturated paper until the surface fibers rub up. This may be done by hand or in a controlled abrading machine.¹² In the mechanical abrading machine, abrasion is carried out by subjecting the sheet to the action of revolving wheels equipped with abrasive rubber wheels while the paper is flooded with water. The test measures a different property than the wet tensile test.

Early Wet-Strength Processes

A large number of processes have been suggested for increasing the wet strength of paper. Many of the treatments involve the addition to the paper of such materials as cellulose acetate, nitrocellulose, ethylcellulose, drying oils, and rubber latex. As a rule, these materials are added in the form of varnishes, and while they increase the water repellency of the sheet and thus exclude water from the inside of the sheet, they do not increase the intrinsic wet strength. Esterification of the fibers on the surface of the paper has been suggested,¹³⁻¹⁵ and it is interesting to note that esterification is effective when carried out on the paper, but is not effective when carried out on the fibers before they are made into paper. None of these processes has attained commercial success.

Vegetable Parchment. When paper is exposed to strong sulfuric acid, the cellulose is gelatinized and the fibers become fused to form a more or less homogeneous sheet. After the acid is washed out, and the sheet is neutralized and dried, a hard, tough sheet results which is resistant to water and even to acids and alkalis. This is probably the oldest type of wet-strength paper, and gives the highest degree and most permanent wet strength. The product is known as vegetable parchment.

Parchment paper made in the above manner has a high degree of both wet strength and grease resistance. It will retain 50 to 60% of its dry bursting strength on soaking in cold water, and will not disintegrate even in boiling water. Greaseproof papers and glassine papers, which are made by conventional beating methods, have good grease resistance, but do not have a high degree of wet strength.

¹² The Taber Abraser, Taber Instrument Corp., Tonowanda, N. Y.

¹³ A. A. New, Canadian Patent 383,849 (Sept. 5, 1939). British 494,253 (Oct. 24, 1938)

¹⁴ W. A. Wiltshire, *World's Paper Trade Rev.* 118, No. 2: 62 (July 10, 1942)

¹⁵ W. A. Wiltshire, *World's Paper Trade Rev.* 128, No. 7, Tech. Supp. 45-48; No. 11: Tech. Supp. 49-56; No. 15: Tech. Supp. 63-68 (Aug. 14, Sept. 11, Oct. 9, 1947)

Use of Proteins and Vegetable Gums. A wet-strength process in fairly wide use comprises surface-sizing paper with animal glue or technical gelatin and exposing the glue-sized paper to high temperature or to a tanning agent such as alum or formaldehyde, or to glyoxal,¹⁶ to render the protein insoluble in water. The optimum pH of the glue solution for obtaining the highest wet strength is said to be about 8.5.¹⁷ Glue is used in this way in the manufacture of blueprint papers where the paper must have sufficient wet strength to resist the soaking which it undergoes in the developing process. The process is not satisfactory for toweling and other similar grades of paper, since it reduces the absorbency of the paper, although Schur¹⁸ has claimed that up to 5% tanned glue can be incorporated in a waterleaf sheet without greatly reducing the absorbency. Casein and other proteins have been suggested for wet-strength treatment, but most processes using proteins are based on the use of glue in combination with formaldehyde.

Two recent patents^{19, 20} describe a wet-strength process utilizing water-soluble mannogalactans such as locust bean gum. In this process, the gum is mixed with the fiber furnish and precipitated by the use of borates or alkaline earth hydroxides. The wet strength obtained is temporary and of value only in those papers such as toweling, where permanent wet strength is not required.

Use of Viscose and Other Water-Soluble Derivatives. Another process for making wet-strength paper involves the use of regenerated viscose. There have been a number of patented processes, including the application of viscose by tub sizing followed by a treatment to coagulate the viscose.^{21, 22} Viscose has also been suggested for application at the beater, after which it is precipitated with acids, acid salts, or heat. There are many operational difficulties in the use of viscose for wet strength development, including corrosion, unpleasant fumes, and special after-treatments, and consequently the process has been very little used. Cellulose derivatives such as the alkyl hydroxy ethers of cellulose which can be dissolved in alkali and precipitated with alum or coagulated by heat have been suggested for wet-strength treatment.²³ Polyvinyl alcohol can be used by treating the sized paper with heat, formaldehyde, or dimethylolurea to produce wet strength. The principle involved in the use of all these materials is based

¹⁶ P. B. Davidson, U. S. 2,414,858 (Jan. 21, 1947)

¹⁷ P. B. Davidson, U. S. 2,414,858 (Jan. 21, 1947)

¹⁸ M. O. Schur, U. S. 2,035,024 (Mar. 24, 1936), U. S. 2,076,599 (Apr. 13, 1937)

¹⁹ M. O. Schur, U. S. 2,215,136 (Sept. 17, 1940); A. K. Smith, U. S. 2,258,628 (Oct. 14, 1941)

²⁰ M. O. Schur, U. S. 2,215,136 (Sept. 17, 1940)

²¹ T. T. Collins and A. Adrian, *Paper Mill News* 72, No. 19: 9-10 (May 7, 1949)

²² T. T. Collins and A. Adrian, *Paper Mill News* 72, No. 17: 26-33 (Apr. 23, 1949)

²³ G. A. Richter, U. S. 2,033,481 (Mar. 10, 1936)

upon the precipitation of a water-insoluble gel on the fibers, so that the fibers are bonded together by means of a water-insoluble bond, although the water absorbency of the sheet is not appreciably reduced.

Use of Formaldehyde. Formaldehyde reacts with cellulose under certain conditions (notably under conditions of high temperature and high acidity) to increase the wet strength (see Ch. I). The reaction presumably results in the formation of cross linkages between adjacent cellulose chains and is thus a true wet-strength development. The treated fibers can take up water, but they are prevented from expanding by the bonds between cellulose chains which are strong enough to hold the chains together in the presence of water. The individual fibers are held together by these same bonds formed between adjacent fibers.

The effect with formaldehyde is believed to be analogous to that which occurs with some of the newer wet-strength resins. However, resins are preferred over formaldehyde because of the high acidity necessary with formaldehyde. This high acidity causes serious embrittlement of the paper due to degradation of the fiber, although part of the embrittlement results, as a natural consequence, from the increase in stiffness of the fiber.^{24, 25} There have been a number of processes proposed for making wet-strength papers by treatment with acid and formaldehyde, but none has attained any degree of commercial success.

Use of Synthetic Resins for Wet Strength

About 1935 a new process for making wet-strength paper was introduced in which a water solution of urea-formaldehyde resin was applied as a surface size, followed by heat curing of the resin in the paper. In 1942, a different process of making wet-strength paper was developed involving the addition of water-dispersible melamine-formaldehyde resin to the beater. Since then, special urea-formaldehyde resins have also been developed for beater addition.

The introduction of synthetic resins completely revolutionized the manufacture of wet-strength papers. With these processes, it became possible to increase the wet strength up to 50% and even more of the dry strength. One of the unusual features of these new wet-strength processes is that the wet strength can be increased without adversely affecting the other properties of the paper. Up to the time these processes were developed, all wet-strength processes involved other major changes in the physical characteristics of the paper, and these changes were often undesirable.

Today, both urea-formaldehyde and melamine-formaldehyde resins

²⁴ I. J. Gruntfest and D. D. Gagliardi, *Ind. Eng. Chem.* 41, No. 4: 760-764 (Apr., 1949)

²⁵ O. B. Hager, D. D. Gagliardi and H. B. Walker, *Textile Research J.* 17, 376-381 (1947)

are used commercially for making wet-strength papers. The melamine resins are applied to the papermaking stock at the wet end only, but the urea resins are used for both beater application and surface application. There is considerable difference between the dry physical properties of surface-treated and beater-treated papers. Both methods tend to increase the dry tensile and bursting strengths, but surface treatment tends to lower the folding endurance, whereas beater treatment tends to increase the folding endurance. The tear resistance of papers treated by either method is generally reduced, but the surface treatment is much more drastic in this respect. Because of the differences in the results produced by the different methods of application, each method will be discussed separately in greater detail.

There is some question whether the reaction between urea- or melamine-formaldehyde resins and cellulose fibers is chemical or physical in nature. Chemists believe that bonds of the hydrogen or covalent type are formed between the resin and the cellulose molecules. Myers and Morin²⁶ have suggested the possibility that the resin (either urea-formaldehyde or melamine-formaldehyde) reacts with glue-like or cementing substances, such as hemicelluloses, in the fibers to form a water-resistant glue upon drying. They found that the retention of urea resin added to kraft pulp in the beaters is independent of the amount of beating. On the other hand, in the case of sulfite pulps they obtained an increase in resin retention with increased beating, and this they attribute to the release of cementing agent from the fibers. In contrast, Taft²⁷ supports the earlier theory that there is a definite chemical reaction between urea-formaldehyde resins and cellulose similar to that obtained between these resins and other polyhydric alcohols such as starch and sugar. The fact that wet-strength resins are more reactive with viscose rayon than with acetate rayon indicates that hydroxyl groups play an important part in wet-strength development, although part of the difference in reactivity can be attributed to lower compatibility of the polar urea resins with the organophilic acetate substance. It has been found²⁸ in textile work that treatment of cotton fibers with urea-formaldehyde resin brings about a change in the dyeing properties of the cotton fiber, causing it to dye more like wool. A similar dye-staining technique useful in testing wet-strength papers for the presence of melamine- or urea-formaldehyde resins will be discussed later.²⁹

Surface Application of Urea-Formaldehyde Resins. The results

²⁶ R. J. Myers and G. V. N. Morin, *Paper Trade J.* 117, No. 23: 241-246 (Dec. 2, 1943)

²⁷ P. B. Taft, *Paper Trade J.* 112, No. 10: 122-126 (Mar. 6, 1941)

²⁸ *Am. Dyestuff Rept.* 25, No. 3: 71 (Feb. 10, 1936)

²⁹ R. W. Stafford, W. M. Thomas, E. F. Williams and N. L. Woodberry, *Paper Trade J.* 120, No. 16: 155-160 (Apr. 19, 1945)

obtained in the surface treatment of paper with urea-formaldehyde resin depend upon the degree of polymerization or molecular weight of the resin used. When urea-formaldehyde condensates of low molecular weight are applied to paper by surface treatment, the resin enters the pores of the fiber where it subsequently undergoes condensation or polymerization to higher molecular weight compounds. In this way, water-insoluble resinous compounds are formed within the pore structure of the fibers. In addition, some of the resin remains on the surface of the fiber, thereby forming water-insoluble bonds at the points where two adjacent fibers are dried in contact with each other. However, with low molecular weight condensates, the bulk of the resin exists within the fiber structure, and consequently has relatively little effect on the physical properties of the paper, such as the amount of fiber bonding, porosity, and absorbency.

Most of the urea formaldehyde resins used for the surface treatment of paper are rather highly polymerized, though still water-soluble, resins. Since the molecular size of the resin is quite large, there is relatively little penetration of resin into the fiber structure.³⁰ Most of the resin remains on the outside of the fibers where it has an appreciable effect on the physical properties of the paper, tending to reduce the absorbency and flexibility of the paper.^{31, 32} As would be expected, the degree of wet strength obtained is appreciably higher than that obtained with the uncondensed or partially condensed resins of low molecular weight which diffuse into the fiber. Most of the urea-formaldehyde resins used for surface treatment are B-stage resins. Non-ionic resins are nearly as effective for surface treatment as the anionic and cationic types.³³

The resin is usually applied in a size press or a size tub. After this, the paper is dried to polymerize the resin and develop wet strength. The curing or condensation of the resin in the sheet is obtained by careful control of the pH, temperature, concentration, and time of reaction. The lower the pH of the resin solution and the higher the temperature of drying, the greater the rate of cure. On the other hand, if the pH is too low or the temperature too high, the resin will precipitate from solution or form a gel before it is applied to the paper. Either ammonium salts of strong acids or alum may be used as catalysts. A suitable formula is given here:

20-30 lb. dry resin
5-10 lb. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (or alum)
100 gal. water

³⁰ I. J. Gruntfest and D. D. Gagliardi, *Ind. Eng. Chem.* 41: 760-764 (1949)

³¹ I. J. Gruntfest and E. M. Young, *Pulp Paper Mag. Canada* 51, No. 3: 190-193, 199, Convention Issue (1950)

³² F. F. Moorehead, *Textile Research J.* 17, No. 2: 96-98 (1947)

³³ M. N. Fineman and I. J. Gruntfest, paper presented at Annual Meeting at TAPPI, New York City (Feb., 1950)

Alum is generally used as the catalyst, since it is effective in two ways, that is, it produces an acid condition and also furnishes aluminum ions which act as a specific catalyst.²⁷ Alum maintains a more or less stable pH in the resin solution.

Ammonium salts such as ammonium chloride or ammonium sulfate function as catalysts in somewhat different fashion. They react with free formaldehyde in the resin solution to form hexamethylene tetramine, and this reduces the concentration of ammonium ions and increases the concentration of anions, thereby lowering the pH . It is this lowering of the pH which promotes the condensation of the resin. The greater the amount of ammonium salt added, the greater the drop in pH , and the more rapidly the condensation of the resin is carried out. The reaction, unlike the effect obtained with alum, is progressive in that the pH tends to drop over an appreciable period of time for any given amount of ammonium salt until the maximum decrease is obtained.

In the surface treatment of paper with urea-formaldehyde resins, the paper should absorb about 40 to 60% of its own dry weight of solution in order to obtain good wet strength. In a typical run on wrapping paper, using a resin solution of 4.5% solids which had been adjusted to a pH of 4.3 with alum, the paper picked up 1.6% resin solids and showed a wet tensile strength which was 36% of the dry strength.³⁴ If 5% or less of resin is applied to the paper, the physical properties of the paper are relatively unaffected, but at higher resin concentrations, harshness and lack of flexibility result.³⁵ Plasticizers can be used to overcome this effect, but they tend to reduce the wet strength.

Urea-formaldehyde resins are sometimes used in combination with starch for surface sizing. Myers³⁵ has pointed out the strong likelihood of a reaction between starch and urea-formaldehyde resin when used in this way. He found under certain circumstances that starch-resin mixtures gave wet-strength values greater than those imparted by the resin alone.

Beater Application of Melamine-Formaldehyde Resins. For all practical purposes, the use of the thermosetting resin polymers for beater addition was started with the introduction of the melamine-formaldehyde resins in 1942. This process was an immediate success and was used extensively during World War II for the manufacture of wet-strength map paper. At present, the resin for this process is sold as a dry white powder which is a low molecular weight condensate of melamine and formaldehyde. Melamine resins usually produce higher wet strengths than urea resins because of their more rapid rate of "cure." They are, however, more ex-

³⁴ Bulletin, "The Uformites for Paper," Rohm and Haas Co., The Resinous Products Div., Washington Square, Philadelphia, Pennsylvania (1947)

³⁵ F. J. Myers, *Paper Trade J.* 110, No. 15: 205-208 (Apr. 11, 1940)

pensive than urea resins. Melamine resin imparts a more permanent wet-strength than the urea resins.

In the preparation of the melamine resin, the resin is first dissolved in water to which a definite amount of acid has been added, and the resin-acid solution is then allowed to age. As a general rule, one mole of low molecular weight condensate (or trimethylol melamine) and 0.8 mole of hydrochloric acid are used. As aging proceeds, the resin condenses into particles within the colloidal range, as indicated by the appearance of a blue haze in the dispersion within several hours. The resin under these conditions is cationic in nature, is infinitely dilutable with water, and is readily adsorbed by paper fibers even in very dilute suspension. The resin solution, when prepared according to directions, ages to the point of maximum effectiveness within three to six hours and remains in this highly effective state for two or three weeks, although the viscosity gradually increases. Eventually, an irreversible gel is formed and the resin becomes of no further value as a wet-strength agent. However, dilution minimizes the tendency to gel, and resin colloids have been kept for years without gelling and with no loss of wet-strength efficiency. Factors which influence the speed of colloid formation and eventual gelation are ratio of resin to acid, concentration of resin, and temperature. Among the changes which take place during the aging of the resin-acid solution, the following are of significance:³⁶ (1) increase in resin particle size, (2) increase in solution viscosity, (3) decrease in stability, (4) loss in surface activity, and (5) decrease in resin particle charge.

The size of the colloidal resin particles is in the range of 20 to 200 Å. (0.2 micron) with the probability that particles even smaller are present.³⁶ The average degree of polymerization is in the neighborhood of 10 to 20, and the average molecular weight lies somewhere between 1,700 to 4,000.³⁷ The most remarkable property, and the one which makes them useful to papermakers, is that they have a positive electrostatic charge.³⁸ This positive charge causes the resin particles to be attracted to and adsorbed by the negatively charged cellulose fibers where they form such a close bond that they cannot be washed free. For this reason, their retention is not dependent upon the presence of alumina or aluminum ions as is the case with rosin sizing. The charge on the particles tends to decrease as the polymer ages beyond a certain point, but this actually aids adsorption, since it reduces the accumulation of surface charge.³⁷

For additions up to 3 or 5% resin on the weight of the fiber, the reten-

³⁶ C. G. Landes and C. S. Maxwell, *Paper Trade J.* 121, No. 6: 51-60 (Aug. 9, 1945)

³⁷ J. K. Dixon, G. L. M. Christopher and D. J. Salley, *Paper Trade J.* 127, No. 20: 455-463 (Nov. 11, 1948)

³⁸ C. S. Maxwell, *Paper Trade J.* 116, No. 19: 207-210 (May 13, 1943)

tion is almost linear,³⁸ but above 5%, a sharp break occurs and practically no additional resin is held, as shown in Figure XII-2. The optimum point seems to depend upon the external surface of the fibers which, in turn, depends upon the amount of beating, since both the retention of resin and the amount of wet strength are increased as the pulp is beaten. Steenberg³⁹ has shown, for a strong sulfite pulp, that the per cent of total adsorbed resin increases from about 22% on unbeaten pulp to over 97% on highly beaten pulp. Maxwell has pointed out that the most effective results with melamine-formaldehyde resins are obtained by adding the resin after the refining has been completed, because this precludes the possibility of opening up new surface within the fiber for which no resin may be available. Myers and Morin⁴⁰ did not find this to be the case with urea-formaldehyde resins (anionic type).

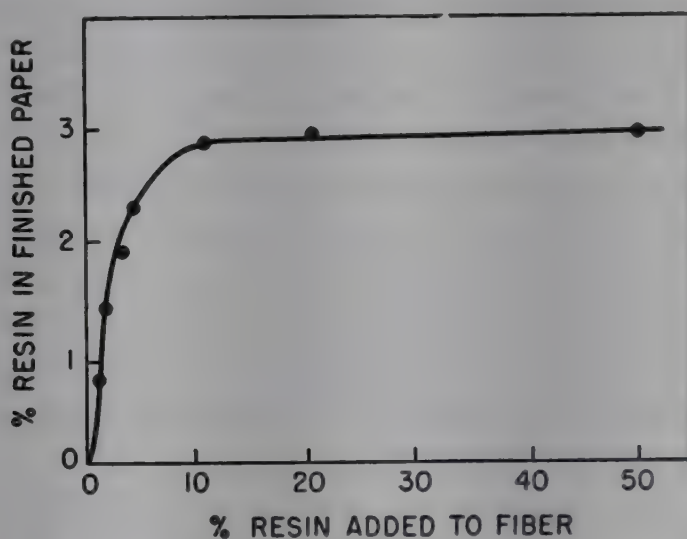


Fig. XII-2. Retention of melamine wet-strength resin in paper as a function of amount of resin added.

Maxwell and Reynolds⁴¹ have found that small amounts of anions are necessary for optimum results with melamine resin colloid, although larger amounts may have adverse effects. In contrast, cations have no measurable effects. The valency of the anion has an important bearing on the amounts necessary to give optimum results. Monovalent anions require about 750 p.p.m., divalent anions about 75 p.p.m., and trivalent anions only a trace. As the divalent sulfate ion (from alum) is the most prevalent ion in most paper mill systems, the concentration of this ion should be controlled so that at the point of resin addition it is about 75 p.p.m. The subsequent addition (after 15 minutes) of more sulfates does not affect the

³⁹ B. Steenberg, *Svensk Papperstidn.* 49, No. 14: 311-323 (July 31, 1946)

⁴⁰ R. J. Myers and G. V. N. Morin, *Paper Trade J.* 117, No. 23: 241-246 (Dec. 2, 1943)

⁴¹ C. S. Maxwell and W. F. Reynolds, *Paper Trade J.* 126, No. 14: 179-183 (Apr. 1, 1948)

resin efficiency. Porter and Lane⁴² found that using aluminum chloride in place of alum increased the efficiency of melamine resin so that 1 per cent resin did the same job as 2 per cent. The increased efficiency was believed to be due to the substitution of chloride ion in place of sulfate ion in the white water.

Maxwell and Landes have indicated that as short an interval of time as possible should elapse between the formation and the drying of the sheet, since the wet strength tends to decrease during this period, possibly because of some change in the resin distribution in or on the fibers.

Under proper use conditions, the results with melamine-formaldehyde are quite remarkable and retention often averages between 60 to 80% of the amount of resin added.⁴³ The cure, or condensation of melamine resin is controlled by the same conditions as affect the cure of urea resin in that it is accelerated by low *pH*, high temperature, and increased storage time before use of the paper. The optimum *pH* for curing is about 4.5, but melamine resins differ from urea-formaldehyde resins in that a moderate degree of wet strength can be obtained at a *pH* as high as 7.0 if other conditions are favorable. In general, the rate of cure is faster than with urea resins, and Steenberg⁴⁴ reports that the wet strength increases linearly with the logarithm of the time of curing in the early stages. Increasing the temperature increases the rate of curing, with 60° C. seeming to be best from a practical standpoint.

Salley and Blockman⁴⁵ have studied the effect of melamine resins on the properties of paper and found that the principal effect is an increase in the amount of adhesion between fibers (both wet and dry). They found⁴⁵ the adhesion to be nearly directly proportional to the amount of resin in the sheet up to about 2% resin. There are several effects, aside from the increase in wet strength, which result from the use of these resins. The dry tensile, burst and folding endurance show marked increases. Other effects are an increase in the slowness of the stock on the wire and an increase in the shrinkage and density of the final sheet.⁴⁶ Melamine resin has a possible favorable effect on the retention of certain fillers, and, as Maxwell has pointed out,⁴⁷ it will, in some sized papers, increase the effectiveness of the rosin or wax sizing.

Beater Application of Urea-Formaldehyde Resins. New types of urea-formaldehyde resins have been developed which are suitable for making wet-strength papers by beater addition. These resins, which are

⁴² C. C. Porter and W. H. Lane, *Tappi* 33, No. 10: 465-467 (Oct., 1949)

⁴³ R. W. Kumler, *Paper Mill News* 66, No. 25: 62 (June 19, 1943)

⁴⁴ B. Steenberg, *Svensk Papperstidn.* 49, No. 14: 311-323 (July 31, 1946)

⁴⁵ D. J. Salley and A. F. Blockman, *Paper-Maker* 64, No. 6: 49-52 (Dec., 1947)

⁴⁶ F. A. Strovink, *Superintendents' Year Book*, pp. 204-215 (1944)

⁴⁷ C. S. Maxwell, *Paper Trade J.* 116, No. 19: 207-210 (May 13, 1943)

sold in both liquid and powder form, can be added directly to the papermaking stock, preferably after the jordan and beater, at such points as the fan pump, screens, or headbox inlet. If the powder form is used, a solution can be made before adding to the stock by dissolving in water at 50 to 60° F. to form a 5 to 10% solution.

The urea-formaldehyde resins are much cheaper than the melamine resins. They do not "cure" so rapidly as the melamine resins and may be retained in the furnish in lower percentage. There are, however, cases where a given job can be done at a lower cost by using urea resins. Generally, from 0.5 to 4.0% urea resin is used on the basis of the fiber furnish.

Varying results, often showing considerable discrepancy, have been reported in the literature for urea resins. This has been due in part to the many different kinds of urea resins which have been used. Therefore, in comparing results reported for urea resins, it is advisable to take into account, wherever possible, the type of resin that may have been used.

The ordinary B-stage urea-formaldehyde resins, which are used for surface sizing, are not suitable for beater addition because of the low retention and the tendency of the resin to precipitate at the high dilutions used. There are, however, several types of urea-formaldehyde resins which are suitable for wet-strength development when the resin is added to the papermaking stock. These are essentially chemically modified B-stage resins which contain added groups on the resin molecule and include the anionic, cationic, and non-ionic types.

The anionic type resins (sulfomethylated resin) are available in water solution, and can be added directly to the papermaking stock, usually after the resin has been diluted to a 5 to 10% solution with water at 50° C. A low pH (4.0–4.5) is required, and a sizable quantity of alum must be added as a mordant to obtain full efficiency. With favorable conditions, the retention may be more than 90% of the resin added at the beater.⁴⁸ The cure of the resin is started at normal drier temperatures, although full wet strength is not obtained until the treated paper has aged for one to two weeks at a temperature of 75° F. or higher. When the absorbency of the paper is a factor, as in paper toweling, the initial pH can be lowered to approximately 4.9 with alum, and further pH reduction brought about by either hydrochloric or sulfuric acid.

Cationic urea resins differ from the anionic type in that they are strongly attracted to the fibers without the aid of alum. This is illustrated by the data in Table I⁴⁹ showing the effect of different wet-strength resins added to the pulp in the presence of no alum and 3% alum on the weight of

⁴⁸ I. Buroztny, *Finnish Paper Timber J.* 28: 207–210 (1946)

⁴⁹ M. N. Fineman and I. J. Gruntfest, paper presented at Annual Meeting of TAPPI, New York City (Feb., 1950)

the pulp. It can be seen that only the cationic resins (urea and melamine) are effective in paper containing no alum. Cationic resins are produced by incorporating polar groups such as the amino and imino groups in the resin molecule through the use of modifiers. The amount of cationic character imparted to the resin should be such that the resin is readily attracted to the fibers, but the cationic charge must not be too great, since this may lead to an early saturation in wet strength effect with only a small amount of added resin if the pulp is only slightly anionic.^{49a} This condition results when the charge on the fibers becomes reversed with only a small amount of adsorbed resin.

TABLE I

EFFECT OF ALUM ON PERFORMANCE OF WET STRENGTH RESINS
IN BLEACHED SULFITE

Type of resin, 3% on pulp	Wet Strength	
	No alum, pH adjusted to 4.0 with HCl	Alum, 3% on pulp
No resin	1.2	1.2
Non-ionic urea resin ^a	1.7	2.4
Anionic urea resin ^b	1.7	3.3
Cationic urea resin ^c	5.3	5.3
Melamine resin (cationic)	4.0	4.4

^a Uformite 414.

^b Uformite 467.

^c Uformite 470.

The results obtained with the cationic urea resins are equal to those obtained with the melamine resin, but it should be pointed out that the values reported are maximum wet-strength values obtained upon oven curing (150° C.) for fifteen minutes. Under normal paper machine conditions, melamine-treated paper would have a higher wet strength upon leaving the machine because of the more rapid rate of cure of melamine resins. Cationic urea resins can be used in sulfite, groundwood, and rag papers to obtain wet strength at relatively high pH values, i.e., 4.0 to 6.5. These resins are particularly valuable for toweling and other absorbent papers where it is desirable to obtain wet strength without the necessity of adding large amounts of alum. However, even with these resins, a low pH is desirable from the standpoint of rapid cure.

Wet strength as high as 40 to 45% of the dry strength can be obtained with 3% urea-formaldehyde resin on the weight of the pulp. Like the melamine resins, the urea resins are more effective on highly beaten, well-hydrated stock than on lightly beaten pulps, but further stock refining after the resin is added is considered undesirable. Unlike the melamine resins,

^{49a} I. J. Gruntfest, *Tappi* 33, No. 11: 529-530 (Nov., 1950)

the results obtained with the cationic urea formaldehyde resins are not affected by the presence of anions. With both types of resins, the presence of fillers tends to lower the wet strength. Other properties of the paper, aside from wet strength, are improved, particularly the burst and tensile strengths, and sometimes the sizing.

Comparison of Pulps for Treatment with Urea- and Melamine-Formaldehyde Resins. Pulps vary in the ease with which they can be effectively treated with urea- and melamine-formaldehyde resins. Anionic wet-strength resins are considered to be more effective on unbleached pulps than on bleached pulps,^{50, 51} and to be more effective on chemical wood pulps than on rag stock, kraft being more effectively treated than sulfite. The cationic wet-strength resins are effective on all types of pulp. For example, using a cationic urea resin, Fineman and Gruntfest⁴⁹ obtained a wet strength which was 53% of the dry strength for a bleached sulfite furnish, compared with a value of only 35% for an unbleached sulfate furnish. The actual wet strength was, however, higher for the unbleached sulfate (7.5) than for the bleached sulfite (5.3). The greater difficulty in treating bleached sulfite pulp with anionic urea formaldehyde resins compared to treating unbleached pulps with these resins may be due to the generally low anionic character of bleached pulps, and to the fact that the anionic character of bleached sulfite pulp, which is primarily due to carbonyl groups, is lost at pH values near 4.^{49a}

The fact that alpha pulps are difficult to treat effectively would indicate that wet-strength resins react with certain substances in the fibers which are found to the greatest extent in the less purified pulps. The possibility of reaction between the resins and part of the hemicellulose fraction has already been mentioned. Bleaching kraft pulp with sodium chlorite has been shown⁵² to decrease the retention of urea-formaldehyde resin to a greater extent than melamine-formaldehyde resin. However, this is probably true only in the case of anionic resins, since commercial cationic urea-formaldehyde resins work very well on thoroughly bleached furnishes. Fineman^{51a} reports that wet strength resins are totally ineffective in pulps from which the hemicelluloses have been removed with alkali.

All other factors being equal, pulps of longer fiber length produce papers of higher wet strength than pulps of shorter fiber length. Certain pulps such as ramie have a very high wet strength, even when untreated,

⁵⁰ I. Buroztyń, *World's Paper Trade Rev.* 130: TS105-111 (1948)

⁵¹ P. Lagally, *Das Papier* 3: 428-434 (1949); through *Paper Ind.* 32, No. 2: 191 (May, 1950)

^{51a} M. N. Fineman, Paper given at the 36th Annual Meeting of TAPPI, New York, N. Y. (Feb. 19-22, 1951)

⁵² G. Schofield and H. A. Harrison, *World's Paper Trade Rev.* 128, No. 15: Tech. Supp. 57-62 (Oct. 9, 1947)

because of their great fiber length. Groundwood pulps are difficult to disintegrate in water, but this is more of a sizing effect caused by the presence of encrusting materials..

Miscellaneous Materials for Imparting Wet Strength

In addition to the above, there are several other agents which have been suggested for imparting wet strength. Some of these are disclosed below.

Polyethyleneimine is a new material which has been used in Germany for beater application for preparing wet-strength papers.⁵³ So far, however, this material has not been used in the United States.

Treatment of paper with organo-silicone resins (e.g., methyl silicon chloride) in the vapor state results in the formation of a thin, evenly distributed, water-repellent film on the surface of the paper.⁵⁴ The paper must be neutralized with ammonia vapors after treatment. This is not a true wet-strength development, since the property imparted to the paper is water repellency. The process was used during World War II for the production of filter papers for gas masks. Ordinary filter papers tend to prevent the passage of air when the paper is wet, due to the closing of the pores in the paper, but silicone-treated papers remain open because the fibers do not wet.

At one time, a synthetic maleic acid resin (a viscous amber-colored 20% solution sold under the trade name of Amberlite W-1) was recommended as a surface sizing agent for wet-strength papers. This resin could be applied under neutral conditions without catalysts, and the paper dried at normal drier temperatures to produce wet strength between 32 to 45% of the dry strength for paper containing about 3% of the resin.^{55, 56} This resin is no longer available commercially.

Permanence of Wet-Strength Bond

The wet-strength bond varies in permanence according to the material or process used to develop the wet strength and the conditions under which the wet-strength paper is stored. The important factors in the storage of the paper are: (1) pH of the paper, (2) temperature and humidity, and (3) degree of cure of the resin. In general, low pH is much more destructive to the wet strength bond than high pH. Britt⁵⁷ found

⁵³ A. F. Tout, *Paper-Maker*, Annual Number, 11-14 (1946)

⁵⁴ W. L. Patnode, U. S. 2,306,222 (Dec. 22, 1942); Canadian Patent 417-363 (Dec. 28, 1943)

⁵⁵ Bulletin, "Amberlite W-1," Rohm and Haas Co., The Resinous Products Div., Philadelphia 5, Pennsylvania

⁵⁶ R. J. Myers and L. E. Kelly, *Paper Trade J.* 127, No. 16: 423-427 (Oct. 14, 1948)

⁵⁷ K. W. Britt, *Paper Ind.* 26, No. 1: 37-44 (Apr., 1944)

that wet-strength paper has its greatest stability at a pH of about 9, as shown in Figure XII-3, where a decided break in the hydrolysis curve is obtained on the acid side of this point and a less pronounced drop on the alkaline side. In obtaining these results the paper was exposed to solutions of different pH for thirty minutes at 200° F. High temperature and high relative humidity are very destructive to wet strength, particularly in the higher ranges. At very low humidities and very low temperatures, there is practically no loss in wet strength upon aging.⁵⁸ The degree of cure is important, because air-dried papers containing wet-strength resin tend to increase in wet strength at first and then, upon continued aging, to decrease in wet strength, whereas heat-cured papers tend to lose wet strength from the very beginning. Typical results are shown in Figure XII-4 for a paper treated with 3.0% melamine resin and aged at 85° F. and 90% R.H.⁵⁸ The heat-cured sample was heated for two minutes at 240° F., while the air-dried sample was not heated at all. As can be seen from

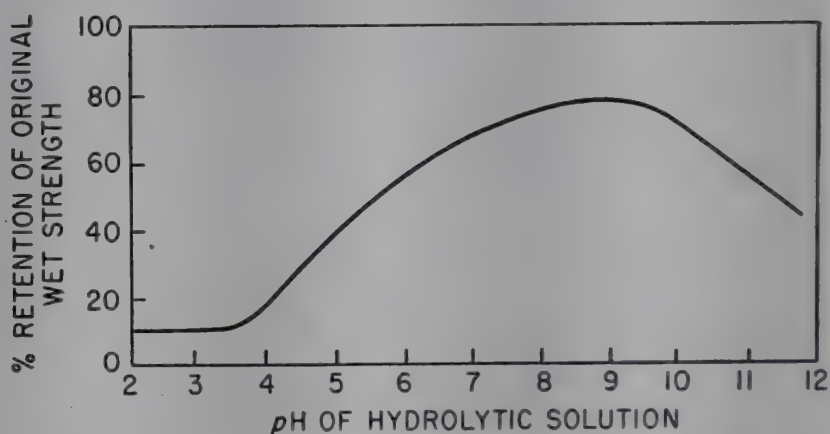


Fig. XII-3. Effect of pH on the stability of wet strength of papers treated with urea-formaldehyde resin.

Figure 4, both papers had about the same wet strength after thirty days, and thereafter lost wet strength at the same rate. The action of micro-organisms reduces the wet strength, but this is the result of attack on the cellulose, rather than attack on the wet-strength bond.⁵⁸

It is well known that wet-strength agents differ materially in the permanence of the wet strength which they impart to paper. The order of permanence of different types of wet-strength treatments is as follows: (1) parchment process, (2) viscose, (3) melamine-formaldehyde, (4) urea-formaldehyde, (5) glue-formaldehyde, and (6) gums such as locust bean and guar.⁵⁸ Melamine-formaldehyde-treated paper has a greater resistance to hydrolysis than urea-formaldehyde-treated paper, and this fact accounts for the more permanent wet strength of melamine-treated paper, especially when stored at high humidity. Under favorable conditions, how-

⁵⁸ C. S. Maxwell and W. F. Reynolds, *Tappi* 33, No. 4: 179-182 (Apr., 1950)

ever, papers treated with urea resins will retain their full wet strength for from six to eight years.⁵⁹ The effects of time and pH of soaking on the wet strength of urea-treated and melamine-treated papers are shown in Table

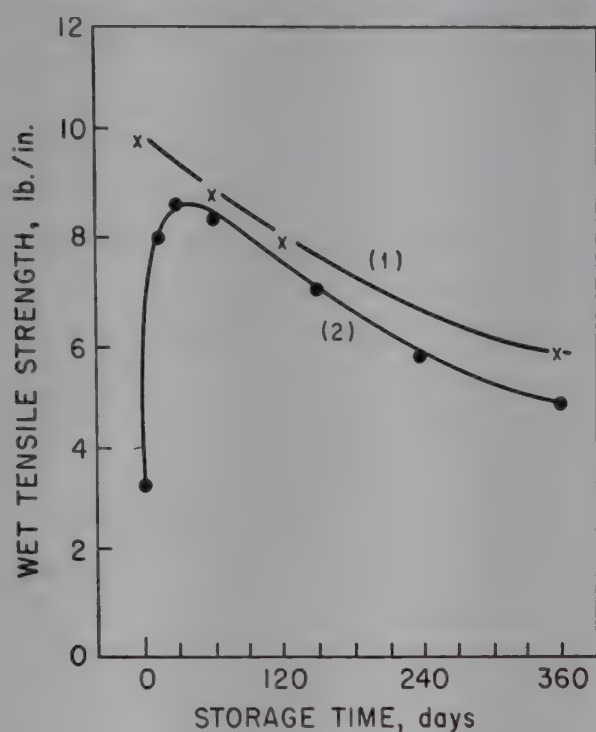


Fig. XII-4. Effect of degree of cure on the permanence of wet strength: (1) heat cured; (2) air dried.

II, taken from work by Brauns.⁶⁰ These results show that both resins are resistant to hydrolysis at a pH of 8.0, but undergo appreciable hydrolysis at a pH of 2.5 to 2.9, the extent of hydrolysis being greater in the case of paper treated with urea resin. A difference of $5^{\circ} C.$ in the temperature of soaking varied the wet tensile strength by about 0.2 kg.

TABLE II

EFFECT OF TIME AND pH OF SOAKING ON THE WET STRENGTH OF PAPER TREATED WITH UREA AND MELAMINE-FORMALDEHYDE RESINS

Time of soaking, min.	Tensile strength of urea-treated paper, Kg.		Tensile strength of melamine-treated paper, Kg.	
	pH of soaking 8.0	pH of soaking 2.9	pH of soaking 8.0	pH of soaking 2.5
5	3.6	3.2	2.9	2.6
30	3.5	2.7	2.8	2.4
60	3.5	2.5	2.8	2.3
240	3.4	2.0	2.7	2.2
1440	3.4	1.4	2.7	1.9

⁵⁹ Private correspondence from I. J. Gruntfest, Rohm & Haas Co. (June 21, 1950)

⁶⁰ O. Brauns, *Paper Trade J.* 129, No. 21: 438-444 (Nov. 17, 1949), translated from *Svensk Papperstidn.*

Utilization of Broke

The utilization of broke from wet-strength papers has been a problem, since the wet-strength treatment makes it very difficult to separate the fibers, even after prolonged soaking in water. However, wet-strength papers can be brought back to the fibrous state by beating in acid medium, since acids hasten the hydrolysis of the resin bonds. The action is primarily a hydrolyzing action resulting from the use of high temperatures and low pH , although some mechanical action is required to defiber the paper after the wet-strength bond has been destroyed. Usually a broke beater, a converted Hollander beater, or a special pulper is used for defibering. The lower the pH and the higher the temperature, the more rapid the repulping. Alum is better than hydrochloric or sulfuric acid, since it results in less degradation of the fibers. Cooking with alkali is not effective in defibering wet-strength papers.

Wet-strength papers made with melamine-formaldehyde are more difficult to defiber than those made with urea-formaldehyde because of the higher rate of cure of melamine resins and because of the greater resistance of melamine resin to acid hydrolysis. Urea resin-treated papers can be readily defibered by cooking at 95° F. and a pH of about 4.5.⁶¹ Papers made with a small percentage of melamine resin can be readily repulped also, but if a high percentage of resin is used, i.e., 3% or more, the conditions required for repulping may be so severe that degradation of the cellulose results. Cooking under pressure at a pH of 4 to 5, or cooking at 185° F. in the presence of a high percentage of alum will defiber broke from melamine resin-treated papers, but some loss in strength occurs.⁶² Johansson,⁶³ on the other hand, reports that cooking at 80° C. at a pH value of 2 does not damage the fibers in the time required for defibering. The best means of repulping wet-strength broke containing melamine resin-treated paper without too much loss in strength is by cooking at about the boiling point (210–212° F.) at a pH of 3.8 to 4.2. A steam-jet process has been suggested⁶⁴ in which nozzles are used for forcing steam at 135 to 150 p.s.i. into the stock between the beater roll and the backfall of a Hollander type beater while the roll is off the bedplate, so as not to beat the fibers. Alum is added to obtain a pH of 3.8 to 4.2, the temperature maintained at 210° F., and the consistency at about 8 to 10%. Papers which have been given a temporary wet strength by the use of glue, monogalactans, etc., do not present any problem in repulping.

⁶¹ L. Henrikson and B. Steenberg, *Svensk Papperstidn.* 50, No. 23: 547–556 (Dec. 15, 1947)

⁶² D. D. Niemeyer and L. V. Forman, *Paper Trade J.* 124, No. 14: 143–150 (Apr. 3, 1947)

⁶³ O. S. Johansson, *Svensk Papperstidn.* 52, No. 6: 131–137 (Mar. 31, 1949)

⁶⁴ M. Goehler, F. H. Reimer and E. F. Davis, U. S. 2,423,097 (July 1, 1947)

Identification of Wet-Strength Resins in Paper

Because of the difficulties in reusing wet-strength papers and the trouble which these papers cause when present, even in small amounts, in waste papers, many suggestions have been made for the easy identification of wet-strength papers. These suggestions include the use of a distinctive water mark on all wet-strength papers, the incorporation of fluorescent dyes in the paper, addition of a small amount of special colored fiber to the paper, and other similar schemes. Bag manufacturers sometimes put a distinctive red or blue stripe on wet-strength papers to aid in identification. However, none of the above methods of marking wet-strength papers is universally used, which means that the burden of identification falls upon the user of waste papers.

The problem of determining whether paper is a wet-strength paper or not is relatively easy. Rubbing the paper with the forefinger after soaking in water or a solution of wetting agent will immediately show up the treated paper, since it will not "rub up," whereas the fibers in ordinary sized papers are easily removed by this treatment. A simple test for detecting the presence of wet-strength resins in paper is based upon qualitative test for nitrogen⁶⁵ and formaldehyde.⁶⁶ If both of these substances are present, it is likely that either urea or melamine-formaldehyde resins were used in treating the paper. The Kjeldahl determination is sometimes used as a quantitative indication of the amount of resin present, although this test is, of course, influenced by the presence of other proteins. See Kjeldahl determination in section on surface sizing with animal glue in Chap. XI.

The problem of determining what type of wet-strength treatment has been given the paper is not so easy, and more elaborate tests are required. The ease with which the paper loses its wet strength in acid media indicates whether urea or melamine resins were used, inasmuch as urea resins hydrolyze much more readily than melamine resins. In this connection, the results of Woodberry and coworkers⁶⁷ show that papers treated with urea resins lose their wet strength in a matter of a few minutes when the paper is boiled in a 0.25% alum solution (pH 3 to 4), whereas melamine-treated papers do not completely lose their wet strength until the paper has been boiled for over two hours.

Dye-staining techniques can be used for differentiating between pro-

⁶⁵ A simple test for nitrogen can be made by fusing a small sample of paper with sodium or potassium and testing for cyanide as Prussian blue.

⁶⁶ A simple test for formaldehyde can be made by hydrolyzing a small sample of the paper by boiling with dilute sulfuric acid and treating the distillate with carbazole-sulfuric acid. A deep blue color indicates the color of formaldehyde.

⁶⁷ R. W. Stafford, W. M. Thomas, E. F. Williams and N. T. Woodberry, *Tech. Assoc. Papers* 28: 275-280 (1945)

teins, urea resins, and melamine resins. The reactions with dyes are based upon the fact that acid dyestuffs are not substantive to cellulose, but they will combine with proteins or protein-like materials such as the urea- or melamine-formaldehyde resins. A suitable test described by Woodberry and coworkers⁶⁸ is based upon the use of an acid dye sold under the name of Calcocid Alizarine Blue S.A.P.G.⁶⁹ The procedure to be followed depends upon the type (if any) of wet-strength material suspected in the paper. Boiling the paper for five minutes in a 0.1% dye solution containing 0.1% sulfuric acid, followed by washing, will show whether wet-strength materials are present at all, since both proteins and resins produce a blue coloration with this treatment, whereas untreated papers remain colorless. Boiling the paper in a 0.1% dye solution containing 1.0% sulfuric acid, followed by washing, differentiates between the melamine and the urea resins, since papers containing melamine resins show a more intense blue color than that obtained with the above method, whereas papers containing urea resin show a less intense blue. Papers containing proteins show varying degrees of blue coloration by this method. Soaking the paper in a 1% caustic soda solution before the treatment with the 0.1% dye solution containing 1.0% sulfuric acid differentiates between papers containing melamine resins and papers containing proteins, since papers containing melamine show an intense blue, whereas papers containing proteins show up colorless.

The identification of melamine and urea resins in wet-strength papers can also be made by preparation of specific crystalline derivatives,⁷⁰ but this is a rather long procedure and is not suited for routine work. The xanthidrol test is specific for urea resins, since xanthidrol condenses with urea to form crystalline derivatives, whereas melamine gives no precipitate. In carrying out this test, the paper is hydrolyzed with acetic acid to form free urea, which is then filtered and reacted with a solution of xanthidrol.⁷¹ The material is then boiled and, if necessary, dissolved and precipitated from pyridine to produce characteristic crystals. According to Widmer,⁷⁰ the crystals are small narrow needles, about 50 to 150 microns long, which are mostly split at the points or taper off at an angle of about 73°. Melamine can be identified by first hydrolyzing the resin-treated paper with acetic acid to produce melamine, which can be identified as melamine crystals by sublimating the residue in the presence of aluminum crystals. Melamine can also be identified as melamine picrate by treating the above solution with picric acid.⁷⁰

⁶⁸ R. W. Stafford, W. M. Thomas, E. F. Williams and N. T. Woodberry, *Tech. Assoc. Papers* 28: 275-280 (1945)

⁶⁹ Supplied by Calco Chemical Division, American Cyanamid Co.

⁷¹ R. W. Stafford, W. M. Thomas, E. F. Williams and N. T. Woodberry, *Tech. Assoc. Papers* 28: 275-280 (1945)

⁷⁰ G. Widmer, *Paper Trade J.* 128, No. 4: 31-34 (Jan. 27, 1949)

COLORING

To be useful, a dyestuff must be able to impart its color to another object. The process of doing this is called dyeing or coloring. It is a physical and colloidal process and is probably the least understood of any of the colloidal processes of papermaking. Most of the colored paper (over 90%) is made by beater coloring.

Increasing the amount of dye in the paper is said to increase the color strength or deepen the color of the paper. If two papers differ only in color strength or depth of color, they can be matched by changing the concentration of dye used. However, a shade difference—i.e., a difference in hue or a difference in dullness—cannot be corrected by changing the concentration of dye, but instead calls for a change in the dye formula.

To understand the dyeing process, it is necessary to understand thoroughly the chemical and physical nature of cellulose fibers, as well as the effects which such added ingredients as rosin, alum, fillers, and starches have on the complex colloidal system. It is also necessary to understand something about the physical and chemical nature of the common dyestuffs, since the various types of commercial dyes react differently with cellulose and are affected in different ways by the addition of alum, rosin, fillers, etc. The mechanism of coloring is thus exceedingly complex, but within recent years much has been learned which is useful to the papermaker about the properties of dyestuffs and their reaction with cellulose in the coloring process. Both the textile industry and the paper industry have contributed greatly to the present knowledge.

An understanding of the reactions taking place between dyestuffs and cellulose is important, not only from the standpoint of the colorist, but also because of the light which these reactions throw on the fine nature of the cellulose fiber. The sorption of dyestuffs by pulp fibers depends on the chemical nature of the dyestuff, the size of the capillary pores of the fiber, and the nature and polarity of the fiber surface.

To understand colors and coloring, the chemist must be familiar with many related fields. The optical properties of the paper are of fundamental importance, and other fields which involve color relationships are bleaching, printing, filling, and coating. Before taking up the various coloring processes, the properties of dyestuffs will be discussed.

Properties of Dyestuffs

A considerable quantity of dyestuffs is used by the paper industry in the manufacture of colored papers. There are three principal methods of adding dyestuffs to paper in the paper mill, namely, addition at the beater along with the rest of the furnish, addition at the size press or at the calender stacks for surface coloring, and addition to pigment coatings for the production of colored coated papers. All these processes use large amounts of dyestuffs. In addition, a number of specialty uses require dyestuffs in lesser amounts.

Water-Soluble Dyestuffs

The principal types of water-soluble dyestuffs used in the paper industry are the acid, basic, and direct dyestuffs. The properties of each of these dyestuffs are discussed in the following sections.

Nature of Dyestuffs. The synthetic dyestuffs derived from coal tar derivatives are the major coloring agents used in the paper industry. Although it is not necessary to go too far into coal tar chemistry, it is important for the paper chemist to have an understanding of the elementary chemical structure and the important colloidal properties of dyestuff molecules. Some degree of understanding of this subject must be attained if the paper chemist is to understand the various reactions which occur in the use of dyestuffs in papermaking.

From the standpoint of the chemist, a dyestuff molecule is composed of a nucleus or arrangement of atoms which is directly responsible for the color and attached substituent groups which affect the hue and dyeing properties. The stability of the color nucleus determines the stability or fastness of the dyestuff to light, heat, oxidizing or reducing agents. Dyestuff chemists have produced many complex arrangements of color nuclei to prepare dyestuffs of different colors. By introducing substituents on the color nuclei, they have been able to change the color intensity or hue of the dyestuff and to control the solubility and dyeing properties. Dyestuffs are usually classified according to their dyeing characteristics, although sometimes they are classified according to color nuclei.

The base of coal tar dyestuffs consists of an aromatic or closed ring compound (e.g., the benzene ring, naphthalene ring, or the anthracene ring). Complicated structures are built up from these bases by the substitution of aminogen radicals (NH_2) for one or more hydrogens on the ring, and by the interaction of these substituted products with one another. When the final products produced by these reactions are highly colored, they may be useful as dyestuffs, if they can be exhausted on papermaking fibers and will meet the required fastness tests.

If a dyestuff owes its solubility to the presence of the aminogen radical

(NH_2), it is classed as a basic dyestuff. If there are enough aminogen groups present, the dye will be soluble in water. Since the aminogen group is quite alkaline, commercial basic dyestuffs are usually made by reacting a simple acid, such as hydrochloric, with the aminogen groups to form salts which are highly soluble in water.

Other groups may be used to confer solubility on a dyestuff radical. The introduction of either phenolic hydroxyl groups or sulfonic radicals (SO_3H) confers solubility when enough of them are present. Because these substituent groups are acid, the dyes are referred to as acid dyes. Commercial acid dyestuffs are usually sodium, potassium, or ammonium salts of the color acid. As a rule, these dyestuffs are highly soluble in water, although this depends upon the number and position of the sulfonic acid groups in relation to the size of the color nucleus. The replacement of sodium or ammonium cations of a soluble acid dyestuff by alkaline earth or heavy metals produces a color salt of reduced solubility. This is the basis of the insoluble color lakes, which are usually calcium, barium, magnesium, or lead salts of acid colors.

When dyestuffs containing the aminogen radical (NH_2) are treated with nitrous acid, combination takes place with the formation of a diazo coupling group ($-\text{N}=\text{N}-$). The products produced in this way can be combined with aromatic amines and phenols to form larger color molecules. The final products are known as azo dyestuffs. These dyes would be insoluble in water if it were not for the fact that sulfonic (SO_3H) radicals are introduced to confer water solubility. Nearly all direct dyes are made in this way (as are many of the acid dyes), and hence most direct dyestuffs are similar to the acid dyestuffs in that they both owe their solubility to acid groups.

It is generally known, but sometimes overlooked in moments of carelessness, that all soluble dyestuffs cannot be mixed together indiscriminately. As a general rule, basic dyes can be dissolved and used together, and acid dyes can be used together, but basic and acid dyes cannot be mixed without precipitation of an insoluble color lake. Acid dyes can be mixed with most direct dyes because of the similarity in chemical constitution.

Commercial dyes are almost never pure, although some of the concentrated basic dyes are nearly pure. In making azo dyes, salt is produced in the chemical isolation of the color from solution, and this salt is left in the color. Sodium chloride or Glauber's salt is often added in standardizing acid and direct dyes, and dextrin is sometimes added for basic dyes. In addition, the color is often shaded.

Dyestuffs are not named after any particular system, although different manufacturers have various general systems of distinguishing between

dyes. The trade name may refer to the class (e.g., basic brown), to the chemical nature (e.g., stilbene yellow), or to the physical properties (e.g., brilliant yellow). Letters following the trade name indicate the color, e.g., R means red, B means blue, G means green, and Y means yellow. A number ahead of the letter generally refers to the strength, e.g., 2R is stronger than R, and 3R is still stronger. Very strong dyes are often marked X, or concentrated. The classification, manufacturer, and color index numbers of American dyes are given in TAPPI data sheets.

Basic Dyestuffs. Basic dyestuffs are salts in which the cation is the dye ion and the anion is an acid radical, such as the chloride, sulfate, acetate, oxalate, or nitrate. Basic dyestuffs are one of the most important classes used in coloring papers. They have the advantage of low cost, high tinctorial strength, and great brilliancy. They are sometimes used in small quantities to improve the brilliancy of acid or direct colors, in this way producing a small amount of an insoluble color lake. When used in this way, they should always be added after the other color. Basic dyes tend to color different types of fibers unevenly in mixed furnishes because of their strong affinity for unbleached pulps and their relatively poor affinity for bleached pulps.

As a class, basic dyes possess poor fastness to light and poor fastness to acids, alkali, and chlorine. They are particularly sensitive to alkali and hard water, and these substances must be avoided whenever basic dyestuffs are used. Any free alkali will tend to form color spots, and calcium and magnesium salts, when present in amounts greater than 50 p.p.m., will also cause difficulties. When making up basic dye solutions, it is customary in some cases to add about 1% of dilute acetic acid to the dye, forming a paste before the water is added. Basic dyes should never be boiled, since this tends to liberate the insoluble color base. As a rule, the temperature of the water should never exceed 200° F., and with a few basic dyes, the temperature should be kept below 160° F.

Acid Dyestuffs. Acid dyestuffs are salts in which the dye ion exists as the acid radical combined with cations, such as sodium, potassium, and ammonium. Acid dyestuffs are more soluble in water than other classes of dyestuffs, and tend to form monomolecular solutions. Solutions up to 8% are frequently used in dip-dyeing paper.

Acid dyestuffs have one advantage over basic dyestuffs in that they do not mottle in mixed fiber furnishes. They have no affinity for cellulose and are only retained on the fiber with the assistance of size and alum. Some acid dyes will migrate when the dyed paper comes in contact with the hot drier roll and cause what is known in the trade as burning on the driers.

Acid dyes have a strong affinity for proteins and are widely used in the textile industry for the dyeing of wool. Many acid dyestuffs give

brilliant shades, and some have a high degree of light fastness, but as a rule, acid dyes have lower tinctorial value and lower brilliance than basic colors and have poor fastness to acid, alkali, and chlorine. Acid dyestuffs can stand considerable heat, and can be dissolved in hot and, in some cases, even boiling water. However, when used in beater coloring, they are generally added dry. As a rule, they are not as sensitive to hard water as basic dyestuffs.

Direct Dyestuffs. Direct colors are sodium salts of color acids similar to acid dyes, but are called direct dyes because of their affinity for cellulose. They are less soluble than acid dyes, tending to form colloidal solutions. They are generally duller. It is possible, however, to dye extremely deep shades by the use of direct dyes.

Direct dyes may be added dry to the fiber furnish, or dissolved in hot water and added from solution. They may be boiled without hurting the color, but this is rarely necessary to obtain a good solution. In general, the maximum solubility is between 1 and 2%, but this varies with the individual color.

As a class, direct dyes have a lower tinctorial value than basic dyes and generally cost more to produce a given shade. Their light fastness is greatly superior to the basic and, in some cases, to the acid dyes. When used with size and alum, however, they form dye-aluminum lakes which usually have a lower degree of light fastness than the dyes themselves. The addition of copper sulfate before the addition of size and alum improves the light fastness of a few direct blues, although the shade is changed somewhat.

Water-Insoluble Colors

A number of water-insoluble (but water-dispersible) colors are used in the paper industry. These include pigments, vat colors, color lakes, and sulfur colors.

Pigments. Pigment colors are obtained from natural mineral sources or from the synthesis of organic or inorganic compounds. Pigment colors were probably the first coloring agents used in the paper industry. They are still used in beater coloring, in paper coating, and in printing inks.

Pigments are sold in either the dispersed or undispersed form. The undispersed pigments are very coarse in size and require grinding to reduce them to an acceptable particle size. Some of the undispersed pigments can be dispersed by the action of the beater and jordan, but ordinarily only the water dispersible types of pigment are used. In no case, however, do pigments approach the degree of dispersion attained with dyestuffs, and pigment particles are always far larger than even the coarsest colloidal particles.

Pigment colors are unlike soluble dyestuffs in that the color of the

dried pigment is the color which is imparted to the paper, and no deeper shade can be obtained than that of the dried pigment itself. The particle size affects the amount of color imparted to the paper, and hence the tinctorial strength of pigment is appreciably affected by the dispersion of the pigment. The coloring power of some pigments is affected by the amount of beating.

Natural Earth Pigments. The natural earth pigments exist already formed in natural deposits. The ore is mined and treated by strictly mechanical processes such as grinding, screening, and air separation. Most of the natural pigments are oxides of iron, the shades of which depend upon the degree of hydration and presence of impurities.

Ochre is an iron oxide which contains a high content of aluminum silicate and other impurities. Ochres range in color from yellow for the highly hydrated oxides to the red-browns for the relatively unhydrated oxides. Burnt ochre is made by roasting to remove the water of hydration. This causes the product to become redder. The siennas are a variety of ochre which are yellow in color. They contain less aluminum silicate than the regular ochres, but are associated with some manganese. Burnt sienna has a deep reddish brown color. The umbers are a variety of ochre which are dark brown in color. They contain a relatively high percentage of manganese. Other natural pigments include ferric oxide (Fe_2O_3), known as red oxide or Venetian red. This pigment is also made artificially by the calcination of iron salts.

Natural pigments are not always uniform in strength or color. They are weak tinctorially and are dull, compared with dyestuffs, but they are fast to light and resistant to the destructive effects of oxidizing agents, acids, or alkalies. Because the individual particles are relatively large, they act very much like fillers, and, when added to paper in large quantities, they tend to weaken the sheet. Natural pigments should always be tested for grit.

Synthetic Pigments. The synthetic pigments are sold in paste or dry form. As a class, they may be divided into two groups, the inorganic and the organic.

The synthetic inorganic pigments used by the paper industry are chiefly metallic salts of inorganic compounds. These are available in a range of yellows, oranges, reds, and blues, and are widely used in printing inks and in beater dyeing and paper coating. Important members of this class are the chrome yellows, which are varieties of lead chromate ranging from yellow-green to yellow-orange in shade, and the cadmium yellows, which are sulfides of cadmium ranging from greenish yellow to reddish orange in shade. Prussian blue, $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$, is a greenish blue pigment made by the precipitation of ferric salt with potassium ferrocyanide. It is fast to

light, acid, and chlorine, but is sensitive to alkali. The so-called soluble Prussian blue is a fine particle size product, large quantities of which are used in the dyeing of paper. This pigment is so highly dispersed that a suspension appears as a true solution (a 1% suspension will pass right through filter paper). Ultramarine is a bright blue pigment made by the calcination of clay, sulfur, sodium sulfate, sodium carbonate, silica, and coal. It is fast to light, alkali, and chlorine, but is sensitive to acid. It is used for coating and for the tinting of high-grade rag content papers.

The synthetic organic pigments have high tinctorial power and, in general, produce bright shades. They have good light fastness and some may be considered permanent color. There are four main classes of synthetic organic pigments, as shown below.

(1) *Pure pigmentary dyestuffs*. These are dyestuffs which are, by their nature, completely insoluble. They are extremely fast to light.

(2) *Concentrated phosphotungstic lake colors*. These are colors produced by the precipitation of soluble basic dyes with complex salts of tungsten and molybdenum (e.g., phosphotungstic-molybdic acid). They are very bright for pigments, but have lower tinctorial values than the soluble dyestuffs. They have good fastness to light and acids, but are not as fast to alkali and chlorine. A highly dispersed form of this pigment is used extensively for tinting many grades of white paper.

(3) *Vat dyestuffs*. These are complex organic compounds which are water-insoluble, but which can be solubilized by reducing with sodium hydrosulfite. In textile dyeing, the vat dyestuffs are generally chemically reduced and dyed in the soluble form, i.e., the leuco form, and then reoxidized on the fiber. In paper manufacture, it is more common to use the colored pigment form, although some work has been done dyeing vat dyes on paper by first reducing the color with sodium hydrosulfite and then reoxidizing onto the fiber. The vat colors have very good fastness to light, acids, alkali, and chlorine. However, they are expensive to use and are more or less limited to use as tinting colors.

(4) *Insoluble lakes or pulp colors*. These are usually calcium or barium salts of soluble monoazoic dyestuffs. They are obtained by the precipitation of the dyestuff with compounds such as barium chloride, calcium chloride, lead acetate, tannic acid, or phosphoric acid. The dyestuffs can be precipitated either alone, or they can be precipitated upon so-called bases. Lakes are usually kept in paste form (hence the name pulp colors), although they may be dried. Lake colors are used in considerable quantities in printing inks, colored varnishes, and wallpaper coatings.

In preparing lakes, the base may be prepared before the addition of the dyestuff solution, or the dyestuff may be precipitated with the base. An example of a simple lake formula is given below:

- 10 g. aluminum sulfate, 5% solution
- 20 g. barium sulfate, water to form paste
- 4 g. sodium carbonate, 5% solution
- 2 g. DuPont Orange II conc., 1% solution
- 11.2 g. barium chloride, 10% solution

The alum is dissolved in the proper amount of water. Sufficient water is

added to the barium sulfate to form a paste, the barium sulfate paste is added to the alum solution, and the mixture is brought to boiling. The soda ash is dissolved in the proper amount of water and brought to a boil, and then the boiling soda ash solution is added to the boiling alum solution. After the precipitate has settled, the supernatant liquor is decanted, and the precipitate is washed several times with water until it is free from sulfates. Next, the dyestuff is dissolved in 100 times its weight of hot water and added to the barium sulfate base, after allowing the temperature to come to 80° C. The dyestuff is then precipitated on the base by adding the barium chloride solution at a temperature of 70 to 80° C. After stirring, the lake is filtered and washed. In the preparation of some pulp colors, tannic acid and tartar emetic may be used.

Other synthetic organic pigments include the phthalocyanines, extremely brilliant green and blue pigments that are permanent to light, and the salts of nitroso-beta-naphthol (a green).

Sulfur Colors. The sulfur colors are an important class of dyes for the textile industry and are sometimes used in the paper industry. These colors are water-insoluble and must be solubilized with alkaline-reducing agents (e.g., sodium sulfide) before they can be used. They have extremely good fastness to light and water, but are generally dull in shade and are used only where light fastness and resistance to water bleeding are a more important requirement than brightness. Their greatest use is in the coloring of brown, black, or olive-drab papers. They are frequently used for dyeing granite fibers for mist effects.

Carbon Black. Carbon black, which is pure carbon, is often considered a synthetic pigment. Carbon black is made by burning hydrocarbon gases in a limited supply of air and collecting the carbon black on steel channels (channel process). Lampblack is produced from the incomplete combustion of oils. Carbon black is used extensively in printing inks and to some extent in beater coloring. It is fast to light, acids, and alkalies.

Identification of Dyestuffs

Frequently the identification label on a dyestuff package becomes lost in the color room, and the paper chemist is asked to identify the "unknown" dye. This is sometimes quite involved, and it is usually best to send the unknown sample to the dyestuff supplier, asking his laboratory to identify the sample. This service is generally supplied by all dyestuff companies and is a relatively simple problem for a laboratory which handles similar problems regularly. The identification may involve one or more of the following: (1) to determine if the dyestuff is simple or mixed, (2) to determine the class to which the dyestuff belongs, and (3) to identify the dyestuff.

To Determine Whether a Dyestuff Is Simple or Mixed. A large number of commercial dyestuffs consist of two or more dyestuffs mixed to-

gether. This mixing of colors is practiced for the purpose of altering the shade of the dyestuff. In a few cases, mixed dyes are used for the purpose of producing a particular color, such as the production of a green by mixing a blue and a yellow dye. To determine whether the dyestuff is a single color or a mixture, the following procedures may be used.

Filter Paper Test. In the filter paper test, a small quantity of the dyestuff is placed on the point of a knife or spatula and gently blown for some little distance onto a piece of wet filter paper. If the dyestuff is a mixture, it will be separated into its component parts, each individual dye showing a different colored spot. Caution should be used to make a light blowout so as to allow the individual dye particles to separate and to dissolve when they hit the paper. The wet sheet of paper should be warmed over a hot plate or over a bunsen burner to warm the water and thereby increase the solubility of the dyestuff.

The blowout should be examined carefully. If all specks are of the same shade, the color is probably a straight color. If there is a large percentage of two or more shades, the sample probably represents a mixture. In examining a blowout, it is advisable to note such factors as the shade of the color, whether the individual dye specks dissolve in water, the apparent rate of solution, and the brilliance of the color produced. All these factors will be leads in the identification of the dye.

Sulfuric Acid Test. In the sulfuric acid test, a small amount of the dyestuff is placed on a knife point and then blown on the surface of some concentrated H_2SO_4 placed in a small porcelain evaporating dish. If the dyestuff is a mixture of two somewhat similar dyes, such as an orange and red, a blowout on filter paper may be difficult to identify, but this method of testing will give quite different color reactions with the acid, indicating that the dye is a mixture.

Dyeing Tests. Some dyes are made by mixing two or more dyes in the wet state, and they therefore cannot be detected by the above tests. Although this is not common practice, it is sometimes done. Such a mixture can be detected by making successive dyeings on cotton, tannin-mordanted cotton, or wool, depending on whether the mixture has been determined to be a direct, basic, or acid color, as explained in the following section.

If the color is a single dyestuff, then a series of dyeings made on the yarn to the point of exhaustion of the bath will show a gradual shading down in strength, but the shade will remain the same. On the other hand, if the dye is a mixture, the first and last dyeings will differ appreciably in shade.

Capillary Test. Another test for identifying mixtures made by mixing dyes in the wet state is by means of the capillary test. In carrying out this test, a sheet of filter paper is mounted between two glass plates, the top one

of which contains a circular $\frac{1}{4}$ -inch hole cut in the center. A cork containing a short length of glass tubing is placed in this hole and the tube filled with a solution of the unknown dyestuff. The dyestuff solution is absorbed by the filter paper, and due to the difference in capillary absorption, each dye in the mixture will form a definite ring or pattern on the filter paper. The various dyes can then be identified by spot tests.

To Determine Class to Which Dyestuff Belongs. The most common method of determining the class to which a dyestuff belongs involves dyeing tests on different types of yarn. For example, acid dyestuffs preferentially color wool fibers, basic dyes color tannin-mordanted cotton, and direct dyes color unmordanted cotton. These differences in coloring properties are the basis for determining the class to which the dyestuff belongs.

In carrying out the tests, a dilute solution of the dyestuff is prepared and a few drops of acetic acid added. A thread of degreased wool and a thread of tannin-mordanted cotton are then added to the dyestuff solution. If the tannin-mordanted cotton is dyed, the color is a basic color. If the wool is dyed, the dye is an acid or direct color.

Tannin-mordanted cotton is prepared by boiling 600 g. of cotton in 2% sodium carbonate for 2 hours. After boiling, the cotton is washed, wrung out, and then added to 25 liters of water containing 3% of tannic acid on the weight of the cotton. The solution is then heated to 93° C., held for 1 hour, steeped overnight, and then wrung dry without washing. The tannin-treated yarn is then added to 25 liters of water containing 1.5% tartar emetic on the weight of the cotton and held at 43° C. for $\frac{1}{2}$ hour, after which it is washed and dried.

Degreased wool is prepared by adding 500 g. of wool to a water bath containing 10 g. of castille soap and 20 g. of sodium carbonate per liter. The bath is heated to 60° C. and held for 3 hours, after which the wool is removed, washed in warm water, and dried.

Next, a thread of unmordanted cotton is placed in the dye solution and warmed, adding a little Glauber's salt (Na_2SO_4). If the cotton is dyed, the indication is that the dye in question is a direct cotton dye. To confirm the test, some of the colored cotton thread should be added to a fresh test tube containing distilled water and boiled to determine whether the thread was really dyed or merely colored mechanically.

If the dye under examination colors both the wool and tannin-mordanted cotton, the trial should be repeated in a very dilute solution of the dye, adding considerable acetic acid. If the dye is an acid dye, it will color the wool; if basic, it will stain the mordanted cotton.

To substantiate whether the dye is basic or acid, it can be tested with tannin reagent. (To prepare tannin reagent, dissolve 25 g. of tannic acid and 25 g. of sodium acetate in 250 cc. of water.) When a few drops of this reagent is added to a dilute (1%) solution of the dyestuff, a precipitate will form if the dyestuff belongs to the class of basic dyes.

The class to which a particular dyestuff belongs can also be determined by small test dyeings on bleached sulfite and unbleached sulfite pulps. Dyeings should be made on both pulps using no size or alum, using alum alone, and using both size and alum. Dyeings are best made in depths of 5 lb. per 1,000 lb. of pulp. Acid dyes will not dye either of the pulps except when size and alum are used. Direct dyes will dye both pulps in all cases. Basic dyes can be identified on the basis of their greater attraction for the unbleached pulps.

Insoluble dyes can be detected on the basis of their insolubility in water when blowout tests are made on wet filter paper. Insoluble dyes may include pigments, sulfur colors, or spirit-soluble dyes. Some of the highly dispersed pigments will at first appear as soluble dyes in this test. A blowout on an alcohol-soaked sheet of filter paper will serve to identify the spirit-soluble dyes.

To Identify the Dyestuff. The identification of an individual dyestuff may be accomplished by a chemical analysis, but the complex nature of most dyes makes such a procedure very tedious, and consequently this method is seldom employed. For practical purposes, identification of dyes is based on the color changes induced by treating the dyestuff with a series of chemical reagents. The color changes induced by adding chemical reagents to the various dyes have been tabulated, and by reference to standard tables, it is usually possible to identify any individual coloring matter. The best known of these reference tables are the Schultz Dyestuff Tables. The dye manufacturer can be of considerable help in this work, and most mills rely upon the manufacturer for identifying unknown dyestuffs.

It is of considerable assistance in dye identification to have on hand authentic samples of the various dyes being used. If there is any question regarding the identity of a certain dye, its reactions can be compared with those of the various known dyes and identification made more quickly.

To Identify Pigments. Pigments can be identified by simple spot tests on the blowout specks on water-wet filter paper. For example, if the spot is destroyed by ink eradicator (3% sodium hypochlorite), the spot is probably due to a sulfur color or possibly iron blue (Prussian blue), a highly water-dispersible blue pigment used extensively in the dyeing of paper. Iron blue is further identified by its extreme sensitivity to alkali, the specks on the blowout being destroyed by spotting with 1% caustic soda. Ultramarine, which is another bright blue color used for tinting some grades of white paper, can be identified by spotting with 1% sulfuric acid. The color is destroyed by acid, but is fairly resistant to alkalies. The phosphotungstic or phosphomolybdic acid salts of basic dyes, which are generally blues, violets, or pinks generally used for tinting white paper, are more resistant to alkalies and acids than Prussian blue or ultramarine, although they

can be destroyed by a warm 2% solution of caustic soda. A more positive identification of the phosphotungstic and phosphomolybdic acid salts of basic dyes is by identification of the metal itself.

The copper phthalocyanine blue and green pigments are quite resistant and will withstand the above chemicals. The vat colors will also withstand these chemicals, but these dyes are rarely used in the dyeing of paper. It may be necessary to ash the dye sample and identify the metal in the ash in order to identify the type of inorganic pigments.

To Identify the Color in Dyed Sample of Paper. A paper mill is frequently requested to develop a colored paper matching the shade of a competitive sample and having the same properties as the competitive sample. One of the best ways for assuring success in this endeavor is to identify the dye used in the competitive sample and to match the shade, using similar dyes. The identification of the color used in a particular sample of colored paper is a more difficult problem than the identification of an isolated dye, particularly when several dyes have been used in the paper. However, it is possible for a trained colorist to identify the dye used in most grades of paper by use of special tests.

Before beginning an identification, it is desirable to know the end use of the paper and the requirements expected of the paper, since this information alone will rule out a large percentage of the commercial dyes. By knowing the type and end use of the paper, it is possible to guess fairly accurately what type of color was used and then determine by analysis whether this guess was correct. The shade, brilliance, and color depth of the competitive paper offer valuable leads to the identity of the dye used in coloring the paper. For example, deep orange shades are usually dyed with the acid oranges for reasons of economy. Most deep shades of red are obtained with purpurine 4B conc. or Congo red, while goldenrod shades are usually dyed with brilliant paper yellow. Unbleached sulfate pulps are generally dyed with basic dyes (with the exceptions noted above), whereas bleached pulps are rarely dyed with basic dyes. Such practical knowledge as this makes it easy for the chemist to learn what types of dyes to expect in a given grade of paper. A few other simple observations which offer valuable leads are as follows:

(1) *Bleeding in alcohol.* All basic dyes will bleed in warm alcohol, but methylene blue and basic brown bleed to a lesser extent than the other basic dyes. The bleed on unbleached kraft is generally less than other stocks. A severe bleed is a definite indication of the presence of basic dyes.

(2) *1% Caustic soda.* A small sample of the colored paper is placed in a test tube with 2 cc. of 1% caustic soda. The solution is boiled for one minute and the degree of bleeding and the effect on shade is noted. Basic dyes are generally destroyed in this test. Prussian blue is destroyed. Some of the acid colors are destroyed, and most acid colors bleed considerably. Brilliant paper yellow is one of the few direct

dyes which bleeds in this test. It also turn a bright scarlet. The stilbene yellows and the yellow SX types turn somewhat redder.

(3) *1% Sulfuric acid.* A boil test in 1% sulfuric acid is handled in the same manner as the alkali test. This test is particularly valuable in identifying purpurine, Congo red, and orange R, since these are acid-sensitive direct dyes which turn blue-black in this test. The blue color of ultramarine is destroyed in the test.

A spot test with 1% hydrochloric acid is helpful, since most acid dyestuffs become deeper in shade when treated with acid, whereas the pigments and most of the direct dyestuffs are not affected. With this test, metanil yellow turns reddish brown, nigrosine turns green, and auramine turns pink.

(4) *3% Sodium hypochlorite (ink eradicator).* A boil test in 0.1% and 3% sodium hypochlorite will differentiate many colors. The yellow SX types, chrysophenine, fast yellow BBL and>NNL, and stilbene yellow are fast to both tests. Fast orange EGL, ERL, and MRL will also withstand both reagents. These soluble colors and the soluble form of copper phthalocyanine (a blue) are the only soluble dyes which will stand this test.

This test does not affect carbon black and is the best test for identifying this color. Molybdate orange and the copper phthalocyanine blues and greens are also not affected, and the phosphotungstic acid salts of basic dyes have fair resistance.

(5) *Light fastness.* A 1-hour Fade-Ometer exposure or a 2-hour sunlight exposure often serves as a valuable lead in color identification. Most basic dyes will show a severe fade under these conditions. Many acid dyes will show some fade. The stilbene or yellow SX types will show a fade to the red and dull side.

(6) *Visual examination.* Visual examination offers valuable leads in color identification. As pointed out above, an examination of the paper to determine the grade is helpful in ruling out the possibility of certain types of dyes. Another visual aid which is sometimes helpful is the degree of two-sidedness, since severe two-sidedness usually indicates that pigment types were used in coloring the paper.

Requirements of Dyestuffs

In addition to the usual requirements for all paper additives, dyestuffs must often meet special requirements, among which are light fastness, waterbleed fastness, alkali fastness, acid fastness, and chlorine fastness. Dyestuffs vary in their ability to meet these fastness requirements, and in selecting dyestuffs and pigments for matching a given shade, the properties of the individual dyes must be taken into consideration to see if they will meet the fastness requirements of the paper at the lowest price.

Light Fastness. The light fastness is a very important property of dyestuffs. Most colored papers are subjected to light, and colors in general tend to lose brilliance and strength on exposure to light. It is impossible to make definite statements about the light fastness of the various classes. As a rule, however, pigments are very fast, direct colors vary from moderate to excellent in fastness, acid colors are slightly poorer than direct dyes, and basic colors nearly always have poor fastness. Sulfur colors have excellent fastness, but are dull.

In the production of those grades of paper where light fastness is important (e.g., wallpapers, seat cover papers, cover papers, and ledger pa-

pers), the stability of the stock should be considered, as well as the light fastness of the dyestuff. Papers made from non-permanent pulps such as groundwood, unbleached sulfite, and unbleached sulfate will deteriorate fairly rapidly and give the appearance of fading, even if expensive light-fast dyestuffs are used.

The amount of fading is, of course, dependent upon the amount of light to which the colored paper is subjected. Sunlight varies greatly in intensity during the year, and summer sun causes far greater fading than the winter sun. Because of the variation in natural light, special instruments, called Fade-Ometers, which use a special carbon arc, are commonly used as a source of standard light for testing the fade resistance of paper. The depth of dyeing should be taken into account in judging fastness, since papers colored in lighter shades appear more sensitive to light than papers colored in darker shades.

Dyestuffs may be graded according to light resistance by first dyeing a standard sulfite stock and then testing the colored paper in a Fade-Ometer and classifying as follows:

Poor	Faded in $\frac{1}{2}$ hour
Fair	Not faded in $\frac{1}{2}$ hour, but faded in $1\frac{1}{2}$ hours
Good	Not faded in $1\frac{1}{2}$ hours, but faded in 3 hours
Very good	Not faded in 3 hours, but faded in 6 hours
Excellent	Not faded in 6 hours

Or, the papers may be tested in natural light by exposing the paper under glass to bright June sunlight and classifying as follows:

Poor	Faded in 1 hour
Fair	Not faded in 1 hour, but faded in 3 hours
Good	Not faded in 3 hours, but faded in 6 hours
Very good	Not faded in 6 hours, but faded in 12 hours
Excellent	Not faded in 12 hours

These methods of rating are used for the conventional papers (e.g., bond) but are not suited for special grades, as, for example, twisting papers which must pass a 100- to 200-hour Fade-Ometer exposure to rate the classification of excellent. The relationship between Fade-Ometer exposure to sunlight exposure at different times of the year is shown in Table I.

Waterbleed Fastness. Waterbleed fastness is an important property on many grades of colored paper (e.g., food wrapping papers, twisting papers, and seat covers) which come into contact with water. Pigment colors are generally very fast to water bleeding. Basic and direct dyestuffs also meet this requirement in many cases, but acid dyestuffs are generally quite poor.

Fastness to Acid and Alkali. Some dyestuffs act as pH indicators, and paper dyed with these dyes may change shade radically when spotted

with either acid or alkali. These dyes are used by the paper industry for reasons of economy, but naturally, they must be used with caution and only in grades of paper where their sensitivity is not a factor.

Typical examples of acid-sensitive dyes are benzopurpurine and Congo red. Paper colored with these dyes will turn a deep blue-black when spotted with a strong acid. These two dyes are so sensitive to acid that they must be dyed at a pH of 6.0 to 7.0 in order to obtain the desired brilliant shade. However, despite this drawback, these dyes are among the most important red dyes used for coloring paper, and most of the Christmas wrapping tissue is dyed with them.

TABLE I

RELATIONSHIP BETWEEN FADE-OMETER AND SUNLIGHT EXPOSURE

Fade-Ometer, hours	Time of year	Average sunlight hours	Bright sunlight hours
1		2.5	1.7
2	June	5.0	3.4
4	July	10.0	6.8
8	August	20.0	13.6
1	April	7.5	3.5
2	May	15.0	7.0
4	September	30.0	14.0
8		60.0	28.0
1		15.0	8.0
2	March	30.0	16.0
4	October	60.0	32.0
8	November	120.0	64.0
1		45.0	11.0
2	December	90.0	22.0
4	January	180.0	44.0
8	February	360.0	88.0

An example of an alkali-sensitive dye is brilliant paper yellow. Paper dyed with this color will turn a brilliant red when spotted with alkali. Consequently, this color cannot be used for soap wrap paper where a chief requirement is fastness to 1% caustic soda. This color should never be used in papers to be pasted with alkaline adhesive, e.g., envelopes, and should not be used in coatings that may be alkaline. On the other hand, it is used extensively for beater dyeing of bond and cover papers where economy, light fastness, and non-two-sidedness are important requirements.

As a rule, natural pigment colors are fast to alkali and acids. On the other hand, some of the manufactured pigments are sensitive to pH changes, for example, Prussian blue, which is bleached white with alkali and therefore

cannot be used in soapwrap or in papers which are to be pasted with alkaline adhesives. Ultramarine is fast to alkali, but is destroyed by acids.

The fastness of colored papers to acid may be determined by spotting the paper with sulfuric acid of 0.1 and 0.5% concentration and allowing the excess liquid to evaporate. The results may be classified as follows:

Poor	A decided discoloration or shade change with 0.1% acid
Fair	A slight discoloration or shade change with 0.1% acid
Good	No discoloration with 0.1% acid, but decided discoloration with 0.5% acid
Very good	A slight discoloration with 0.5% acid
Excellent	No discoloration with 0.5% acid

The fastness of colored papers to alkali may be determined by spotting the paper with a 2% solution of soda ash and a 1% solution of sodium hydroxide, the excess liquid being allowed to evaporate. The results may be classified as follows:

Poor	A decided discoloration or shade change with 2% soda ash
Fair	A slight discoloration or shade change with 2% soda ash
Good	No discoloration with 2% soda ash, but a decided discoloration with 1% caustic soda
Very good	A slight discoloration with 1% caustic soda
Excellent	No discoloration with 1% caustic soda

Chlorine Fastness. Chlorine fastness is an important consideration, because most ink eradicators contain chlorine as sodium or calcium hypochlorite. Chlorine-sensitive dyes are used for coloring certain safety papers, but in ledger and other business papers, they are not practical.

Nearly all pigments are quite fast to chlorine, but dyestuffs are, as a rule, quite sensitive to chlorine. Some of the direct yellows and a few of the direct oranges are fast to ink eradicator, but most other soluble colors are destroyed by it. Vat colors are fast to chlorine.

The fastness of colored papers to chlorine can be determined by spotting the paper with calcium hypochlorite solution containing 0.01% and 0.15% of available chlorine, the excess liquid being allowed to evaporate. The results are classified as follows:

Poor	Color destroyed with 0.01% solution
Fair	A slight change with 0.01% solution
Good	No change with 0.01% solution, but a decided change with 0.15% solution
Very good	A slight change with 0.15% solution
Excellent	No change with 0.15% solution

Some mills frequently limit themselves to the use of dyes that are sensitive to bleach. This is done purposely so that the colored broke can be bleached, thus eliminating the necessity of storing for future use.

Coloring with Acid, Basic, and Direct Dyestuffs

In order to obtain full value from a dyestuff, it must be retained in the sheet in such a form that its full color is developed. The amount of dyestuff which must be retained in paper to obtain color is very small. Sigvardt¹ has estimated that only about 0.001 mole of dye per 100 g. of fiber, or 0.4% dye, is required to produce a sheet of high tinctorial strength in an average commercial dyeing with a basic dyestuff.

Retention of Dyestuffs in Paper

The exact mechanism for the retention of dyes in paper is not known. This is different for basic, acid, and direct dyestuffs, and consequently must be explained separately for each of these classes. Also, individual dyes in a single class have widely different dyeing properties. Most dyeings are reversible under the conditions of the dyeing reaction, with the point of equilibrium differing greatly with different dyestuffs. During the coloring process, conditions are chosen which favor fixation of the dye upon the fiber, but later during use, conditions may not be so favorable, and the dye may tend to wash from the paper when wet with water.

Harrison² found that the Freundlich adsorption equation represents the retention of dyestuffs for all three classes of dyestuffs, i.e., the relationship between the logarithm of the weight of dye adsorbed and the logarithm of the weight of dye left in the white water is a straight line; or, the dye adsorbed is proportional to C raised to the $1/n$ th power where C is the amount of dye unadsorbed and n is a constant. This relationship shows that an increase in the dye concentration increases the amount of dye adsorbed by the fiber, but at a lower rate than would correspond to a linear relationship.

One type of force which may be operative in the fixing of dyes on cellulose fibers is the force due to electrostatic charge. Since cellulose fibers normally carry a negative electrostatic charge in water suspension, they tend to attract and hold dyestuff particles which are positively charged. On the other hand, if cellulose fibers are given a positive charge by treatment with alum, they will attract and hold negatively charged dye particles. Acid dyes are negatively charged and hence have very little attraction for cellulose with its normal negative charge. This can be illustrated by dipping untreated paper in a weak solution of a pure acid dyestuff. On the other hand, changing the charge on the fibers from a negative one to a positive one by impregnating the paper with positively charged aluminum hydrate causes the paper to become deeply colored, since it now attracts negatively charged dye ions. The reverse is true when basic dyes are used.

¹ C. M. Sigvardt, *Paper-Maker* 110, No. 6: TS 55-61 (Dec., 1945)

² W. D. Harrison, *Paper Trade J.* 105, No. 13: 179-185 (Sept. 23, 1937)

Much has been learned about dyeing from the experience of the textile colorist. However, conditions of coloring are often quite different in the textile industry from those which exist in the paper industry. For example, direct dyes are widely used in both industries, but in the textile industry they are usually applied from solutions at higher temperature (130° F.) and in the presence of higher salt concentrations than are used in the paper industry. In the paper industry, a great deal of dyeing is simply lake production, that is, the formation of an insoluble dye by precipitation of the dye with alum. Obviously, a reaction such as this involves a minimum of interaction between the fiber and the dyestuff.

Penetration of Dyestuffs into Fiber

The internal surface of papermaking fibers is, of course, much greater than the external surface, and much of this internal surface is probably available for dyeing. Certain colors are well enough dispersed to penetrate into the submicroscopic pore structure of the fibers, particularly the basic and acid dyestuffs. Many of the direct dyestuffs exist in aggregates too large to penetrate the pores of the fiber unless they are heated to break up the aggregates.

During the coloring process it is likely that the dye molecules diffuse into the fiber pores, where they repeatedly collide with the pore walls as a result of thermal agitation. If the dye molecules have a chemical nature such that they are strongly attracted by the cellulose or other constituents of the fiber, they will tend to adhere to the pore walls, but if not, they will rebound from the walls and eventually diffuse out of the pore. Because there are so many more points of attractions within the pores than on the outside of the fiber, those dyestuffs which can penetrate the fiber and be retained there are the most effective and produce the most stable dyeings.

Some authorities believe that orientation of dyestuffs takes place on the surface of the cellulose crystallite, although x-ray pictures do not show it. Wiley³ states that cellulose fibers colored with certain dyestuffs exhibit optical anisotropy in the form of dichroism (a difference in the ability of the fiber to absorb polarized light depending on the angle between the plane of polarization and the fiber axis), which he believed to be caused by an oriented adsorption of dyes on the oriented cellulose structure.

Coloring with Basic Dyestuffs

Basic dyes have only a slight affinity for pure cellulose, and it is virtually impossible to obtain complete exhaustion of basic dyes on bleached rag and alpha pulps in beater dyeing. These dyes, however, have a very strong affinity for unbleached and groundwood pulps. The affinity of these dyes

³ P. R. Wiley, *Am. Dyestuff Repr.* 33, No. 5: 95-98 (Feb. 28, 1944)

for the fiber increases in direct proportion to the amount of lignin and other impurities present, and it has been pointed out that there is a direct relationship between the affinity of basic dyes for the fiber and the permanganate number. The difference in affinity for bleached and unbleached pulps may be clearly illustrated by preparing a laboratory mixture of 80% alpha pulp and 20% unbleached sulfite and adding 1/10% Malachite green. The color will be found to "jump onto" the unbleached fiber, leaving the bleached fiber practically colorless and producing a severe degree of "graniting" in the sheet.

It is for the above reason that basic dyes are used almost exclusively for dyeing groundwood and unbleached pulps and are rarely used for dyeing bleached pulps. In general, basic dyes may be used to obtain deep and brilliant shades on unbleached pulps at low cost, even without the addition of size and alum. Special precautions must be taken when dyeing mixed furnishes to eliminate graniting, and for this reason basic dyes are generally not used for dyeing mixed furnishes of bleached and unbleached pulps, since acid dyes are much more suitable.

In dyeing bleached pulps with basic dyes, the use of mordants is frequently resorted to. A mordant is selected that has an affinity for cellulose and will precipitate the basic dye. In this way a dye lake is formed directly on the fiber. Tannic acid or a complex formed from tannic acid and tartar emetic are frequently used as mordants. Recently some of the dyestuffs manufacturers have introduced synthetic mordants which are generally somewhat cheaper. These mordants dull the shade, although they materially improve the exhaust of the dye and also increase the waterbleed fastness of the finished paper. It is believed that one of the reasons groundwood fibers are colored so readily with basic dyes is the presence of lignin which reacts with the dye to form an insoluble lake. Mordants should be added with the dye, before the size and alum.

If basic dyes must be used in mixed furnishes, mottling can be reduced by adding the dye to the bleached pulp first, and then adding the unbleached pulp later to prolong the time of contact with the bleached pulp as long as possible and reduce the time of contact with the unbleached pulp. Another method which is widely used to improve the uniformity of dyeing in mixed furnishes is to add the rosin size and alum to the beater before the color is added, thus reducing the affinity of the dye for the unbleached pulp. Apparently the rosin particles in the fiber slow up the fixation of color and thereby permit more even dyeing. Mottling may also be reduced by adding selected mordants (the sodium salt of the condensation product of naphthalene sulfonic acid) to the pulp before the color. Still another method is to mix the dyestuff with clay before adding to the beater. Adding the dye

cold and in very dilute solution also tends to reduce mottling. As a rule, basic dyes should be dissolved before adding to the beater.

Other factors which are of importance in dyeing are the temperature and pH of the stock and the time the dyestuff is in contact with the fiber. These will be discussed later. In general, temperature and pH are of less importance in coloring with basic dyestuffs than with other classes of dyestuffs, since basic dyes are little affected by changes in pH within the range of 4.5 to 6.5, although their retention is poor at the neutral point.

The dyeing mechanism with basic dyestuffs is very interesting and sheds considerable light on the structure of pulp fibers. The reaction is ascribed by some to a chemical combination between the basic groups of the dyestuff with the acid groups (carboxyl, sulfonic acid, or phenolic hydroxyl) of the fiber constituents.⁴ Thus, in the coloring reaction the basic dye may be taken up by the fibers in such a way that the organic dye radical is retained, leaving the acid radical in solution, as illustrated by the following equation:



The reaction is reversible, and when equilibrium is reached, no more of the dye will be adsorbed by the fiber. Alum or any other acidic material tends to shift the equilibrium to the left, and hence interferes with the dyeing reaction.⁵ The reaction may take place on the surface of the cellulose crystallites, since basic dyes are dispersed well enough to penetrate the intercrystalline pores of the fiber.

Normally, true cellulose contains very few acidic groups and, as a result, has very little affinity for basic dyes, although Sigvardt⁶ believes that even highly purified cellulose contains some carboxyl groups which will react with basic dyes. On the other hand, commercial unbleached pulps contain a large number of available carboxyl groups which may exist in the cellulose itself, in the hemicellulose fraction, or in the lignin. Lignin contains an abundance of acid groups, such as the hydroxyl groups in native lignin and the sulfonic acid groups in the lignin of unbleached sulfite fibers, and consequently lignin plays an important role in the fixing of basic dyes. With the latter group, the dye is adsorbed as a result of ion exchange whereby the calcium ion of the calcium sulfonate lignin is replaced by the dye base, according to the above equation. Basic dyes are strongly adsorbed by lignified fibers and give dye retentions in the neighborhood of 85% or above.⁷ Because of the effect of the sulfonic acid groups, sulfite pulps having the same lignin content as soda or sulfate pulps absorb twice as much

⁴ W. D. Harrison, *Paper Trade J.* 105, No. 13: 179-185 (Sept. 23, 1937)

⁵ R. E. Rose and J. C. Schmidt, *Paper Trade J.* 101, No. 5: 55-58 (Aug. 1, 1935)

⁶ C. M. Sigvardt, *Paper-Maker* 110, No. 6: TS 55-61 (Dec., 1945)

⁷ W. D. Harrison, *Paper Trade J.* 105, No. 13: 179-185 (Sept. 23, 1937)

dye,⁸ although the affinity of basic dyes for all unbleached pulps and ground-wood is excellent. Sigvardt believes that the complexes formed between basic dyes and sulfonic acid groups are more stable than those formed with either the phenolic hydroxyl groups of normal lignin or the carboxyl groups of cellulose, the latter being the least stable of all.

In the preceding paragraphs, the mechanism of dyeing with basic dyes has been explained on the basis of a chemical reaction between the dyestuff base and the acid groups located in the lignin molecule. Coloring with basic dyestuffs can also be explained by the electrostatic charge theory. This latter theory is based on the property of basic dyestuffs whereby they ionize to produce positively charged ions in solution. Since pure cellulose fibers have a weakly negative charge, there is only a slight mutual attraction between the dye and the fibers. Bleaching increases the negative charge on the fibers and hence increases the attraction for the dye to a slight extent. On the other hand, the presence of alum reduces what little attraction there is, because the alum is preferentially adsorbed, due to its stronger positive charge, thereby reducing the negative charge on the fibers. Although these effects are of importance on highly purified pulps, they are almost completely overshadowed on pulps containing an appreciable amount of lignin because of the strong tendency for basic dyes to react with this natural mordant.

Cellulose has no appreciable fixing action on basic dyes, and consequently the dye molecules are free to diffuse into the fiber until they come into contact with lignin or another mordanting agent to which they are attracted. Since the dye base tends to become fixed where it contacts an acidic group in the lignin molecule, uneven dyeing or graniting is often the result. Thus, as previously explained, basic dyestuffs usually produce mottled effects in mixed furnishes of bleached and unbleached pulps because of their weak attraction for the bleached pulp and their strong attraction for the unbleached pulp.

Coloring with Acid Dyestuffs

As a rule, acid dyestuffs are highly soluble compounds and exist in solution in the form of a monomolecular dispersion. They have no affinity for cellulose, and both rosin and alum are necessary for the best retention of acid dyestuffs. In cases where deep shades are required, it may be necessary to use more size and alum than normal, but too much alum should be avoided because it tends to deaden the shade, particularly with metanil yellow. Acid dyes should be added either before the size and alum, or after the size and ahead of the alum. Even under the best conditions, the white water is usually highly colored, and as a rule the color is loosely bound to the fibers, giving the colored paper poor fastness to water. Because acid

⁸ C. M. Sigvardt, *Paper-Maker* 110, No. 6: TS 55-61 (Dec., 1945)

dyestuffs have no natural affinity for cellulose or lignin, they generally produce even dyeings on sized paper and do not cause graniting like that obtained with basic dyestuffs. However, they tend in some cases to mottle and burn on the driers, particularly with heavy papers and paperboards.

It is believed by some⁹ that acid dyestuffs are held in paper through the formation of an insoluble color lake resulting from the reaction of the dyestuff with alum. According to this theory, the color radical is believed to react with aluminum ions to form an insoluble compound, which is then attracted to the fiber and adsorbed there. Under these circumstances, the dyestuff as it exists in the paper would be an insoluble aluminum salt of the color nucleus. It should be pointed out, however, that very few acid dyes can be retained with alum alone, and that the size-alum complex is required to hold acid dyes. The more soluble acid dyestuffs do not form sufficiently insoluble compounds with alum to be retained well in the beater.¹⁰

Coloring with acid dyestuffs may also be explained by means of the electrostatic charge theory as follows. Both the dye acid and the cellulose fibers are negatively charged, and therefore mutually repel each other. However, if alumina floc is formed, the positively charged alumina is adsorbed on the fibers first, giving them a positive charge, after which the dye is attracted to the fiber; or, the alumina may react with the dye first and the resultant dye-alumina complex with its positive charge, will then be attracted to the negatively charged fiber. Some observers believe that the complex formed in the latter way between the alumina and dyestuff involves a displacement of the sulfate ion normally adsorbed on the alumina by the color anion. If such is the case, it would be desirable to precipitate the alumina as far on the acid side as possible to increase its positive charge. It is also desirable to use acid dyes in which the colored anion carries two or more negative charges, since Miller¹¹ suggests that acid dyes containing divalent and trivalent colored anions react with alumina, whereas monovalent dye anions will not.

Because of their solubility, acid dyes may be added dry to the beater. The *pH* is important, and a *pH* within the range of 4.5 to 5.5 generally gives best results. Considerable loss in coloring value results if the *pH* is increased toward the neutral point. Temperature seems to have very little effect on the retention of acid dyes.

It is possible to improve the water fastness of paper dyed with acid dyes by the use of certain salts which may be added to the beater after the acid dyestuff, or applied to the surface of the colored paper. Metallic cations such as calcium, magnesium, and lead, will replace the more soluble

⁹ R. E. Rose and J. C. Schmidt, *Paper Trade J.* 101, No. 5: 55-58 (Aug. 1, 1935)

¹⁰ E. R. Laughlin, *Paper Ind.* 24, No. 5, 6, 7, (Aug., Sept., Oct., 1942)

¹¹ L. B. Miller, *Paper Trade J.* 108, No. 2: 18-24 (Jan. 12, 1939)

cations from the acid dye and result in a color of decreased solubility in much the same way that alum insolubilizes the dyestuff by forming a relatively insoluble aluminum salt in the beater. Certain synthetic resins may be used for the same purpose.

In contrast to their low affinity for cellulose, acid dyestuffs have a very strong affinity for most proteins and are widely used in the textile industry for the dyeing of wool. The mechanism probably consists of a neutralization of basic groups in the protein molecule by the acidic groups of the dye molecule. The affinity is very high, since the dyestuff is held by very tenacious forces involving both secondary and primary valence forces.¹² By the use of acid dyestuffs, it is possible to distinguish between papers which have been treated with proteins or protein-like materials, such as animal glue, urea-formaldehyde resins, or melamine-formaldehyde resins, and papers which contain no protein or related material.¹³

Coloring with Direct Dyestuffs

Direct dyestuffs have a strong affinity for cellulose and can be used without the assistance of rosin size or mordants. In fact, bleached and highly purified fibers seem to have slightly greater affinity for direct dyestuffs than highly lignified fibers. Because of their high degree of substantivity, or affinity for cellulose, paper stocks treated with direct dyestuffs usually take up the color completely in a short time and show a minimum of two-sidedness. However, because of their natural affinity for cellulose, direct dyes tend to color preferentially the first fibers with which they come into contact, causing graniting. This is more pronounced when coloring light shades, but can usually be overcome by using dilute solutions or by adding the dyestuff dry to the beaters. Another expedient is to add the dyestuff to the beater after the rosin size, since the alkaline size retards absorption of dye by the fiber.

Direct dyes are widely used for the coloring of waterleaf or blotting papers, using bleached pulps without alum. Very deep shades can be obtained in this way. When used for deep shades on unsized papers, the addition of sodium chloride increases the retention, and in most cases, heating the stock increases the depth and brilliance of shade. Commercial practice calls for the use of about 50 to 100 lb. of sodium chloride per 1,000 lb. beater, or about 5 to 10% salt on the weight of the fiber, and heating of the beater to a temperature of 100 to 140° F. The practical papermaker knows that this increases the "exhaust" and improves the dye retention. If the dye is dissolved hot, it should be cooled before adding to the beater to prevent graniting.

¹² R. E. Rose, *Rayon Textile Monthly* 23, No. 5: 287-288 (May, 1942)

¹³ R. W. Stafford, W. M. Thomas, E. F. Williams and N. T. Woodberry, *Paper Trade J.* 120, No. 16: 155-160 (Apr. 19, 1945)

Sodium carbonate and sodium aluminate improve the brilliancy of some direct dyestuffs and may be used where they do not otherwise interfere with the sizing. It is customary to use these alkalies with certain direct dyes to raise the pH so that the maximum brilliance of the dye is obtained. Some of the direct dyes are very sensitive to hard water.

The retention of direct dyestuffs can be increased through the use of rosin size and alum. Alum results in improved dye retention and undoubtedly results in a different method of retention from that obtained in the coloring of papers containing no alum. In the presence of alum, the effect resembles that obtained with acid dyestuffs, which means that the dye is fixed on the outside of the fiber rather than within the fiber. However, the use of alum with direct dyes reduces the brightness and fastness to light. Since direct dyestuffs are precipitated by alum, they should be added to the beater before the alum. If added after the alum, they do not show their full strength, inasmuch as they are precipitated before they become thoroughly mixed with the fibers. This reactivity of direct dyestuffs with alum makes it difficult to add the dyestuff directly to the stock chests in cases where it is desirable to change or deepen the shade on short notice,¹⁴ but this can be done by adding the dye in a very dilute and cold solution. Two-sidedness often results if direct dyes are added after the alum.

Direct dyes resemble acid dyes in many of their chemical properties. However, direct dyestuffs are, as a rule, much less soluble and generally form colloidal solutions consisting of aggregates of dye molecules, in contrast to the monomolecular solutions of most acid dyestuffs. It has been stated that the substantivity or affinity of direct dyes is related to their tendency to associate into large aggregates.¹⁵

Direct dyestuffs have been used for many years in the textile industry and the process is well understood, but it is quite likely that the same mechanism is not utilized in the dyeing of paper, except possibly in the coloring of waterleaf papers when only salt and heat are used. In textile coloring, the dyeing solution contains salt in high concentration, and the dye is applied at very high temperatures (just below the boiling point). Both high temperature and high salt concentration are essential to the rapid and complete dyeing of textiles, and under these conditions the dye molecules penetrate into the fiber structure and attach themselves to the walls of the pores. Swelling of the cotton fiber is essential in the process in order to open up the intermicellar spaces for penetration of the dye particles, and surface-active agents are often used for this purpose. Fibers treated with a small amount of wet-strength resin (urea-formaldehyde) do not absorb direct dyes, since swelling of the cellulose chains is inhibited by cross linkages.¹⁶

¹⁴ J. R. Roberts, *Paper Ind.* 24, No. 9: 941-943 (Dec., 1942)

¹⁵ S. Lenher and J. E. Smith, *Ind. Eng. Chem.* 27, No. 1: 20-25 (Jan., 1935)

¹⁶ I. J. Gruntfest and D. D. Gagliardi, *Textile Research J.* 17, No. 11 (Nov., 1948)

Direct dyes have an optimum particle size above which they become too large to penetrate into the submicroscopic pores of the fibers. This has been estimated to be a size¹⁵ of 17 to 20×10^{-8} cm., which is about the estimated size of the pores in the fiber. High temperature aids in the absorption of direct dyes by decreasing the particle size and permitting penetration into fiber. In this connection, it might be pointed out that direct dyes seem to be the only type where retention is affected from a practical standpoint by temperature. The effect of salt is not so well understood, but it is known that salt lowers the solubility of direct dyestuffs over the whole range of concentration¹⁷ up to the point where the dye is salted out of solution. Rose^{18, 19} visualizes the process of coloring with direct dyestuffs in the textile industry as taking place in the following stages. First, the dyestuff, which is in a monomolecular state at the high temperature of application, readily diffuses into the intramolecular pores of the cotton fiber where it becomes anchored. The high electrolyte concentration on the surface of the cellulose may be responsible in part for the aggregation of the dye molecules on the cellulose surface, and the added salt probably supplies the remaining electrolyte needed for this aggregation. Lowering of the temperature causes the dyestuff to aggregate into particles which are too large to migrate back through the pores of the fiber, and the dyestuff is said to be fixed. Those direct dyes which tend to aggregate most on cooling give the most effective dyeings against washing.

Coloring with Pigments

Pigments have a few advantages over soluble dyestuffs for the coloring of paper, the most important being their good fastness to light and other destructive agents. On the other hand, they have many disadvantages. They are generally weak tinctorially, which makes it necessary to use higher percentages than required with soluble dyestuffs. Because of their relatively large particle size and the relatively high percentages required, pigments have somewhat the same effect as fillers in that they tend to weaken the sheet. Some pigment colors may contain grit, which acts as an abrasive on the felts and wires. In general, pigments produce a very two-sided effect.

Practically all the pigments used today are of the water-dispersible type and can be added dry to the beater. A few of the tinting pigments are prepared in suspension, but even this practice is disappearing. As a general rule, only the water-dispersible types of pigments should be considered,

¹⁷ F. L. Usher and A. K. Wahbi, *J. Soc. Dyers Colourists* 58, No. 11: 221-228 (Nov., 1942)

¹⁸ R. E. Rose, *Rayon Textile Monthly* 23, No. 4: 217-218 (Apr., 1942)

¹⁹ R. E. Rose, *Rayon Textile Monthly* 23, No. 3: 161-163 (Mar., 1942)

since the other types do not wet out or disperse, but instead float on the surface.

Retention of Pigments

Colored pigments are held in paper by the same forces which are operative with the white pigments used in filling. They have no affinity for cellulose and ordinarily show a low retention when used in unsized papers. They can, however, be used for coloring waterleaf or blotting papers if alum is used. Their properties of imparting opacity and their light and heat fastness make them well suited for coloring unsized impregnating papers for laminates where these properties are required in a high degree.²⁰

Because of the relatively large size of pigment particles, mechanical retention is a greater factor with pigments than with soluble dyestuffs. Alum is essential in obtaining satisfactory retention, and the retention usually increases as the amount of alum is increased up to a certain point. In addition, increasing the amount of alum appears to strengthen the bond between the fiber and the pigment, even after the maximum retention has been obtained.²¹

The retention of pigments can be explained by the fact that pigment particles take on an electrostatic charge when suspended in a polar medium such as water. This charge varies in intensity according to the chemical constitution of the pigment, but it is always negative (the same as cellulose), and therefore the pigment and fiber tend to repel each other. When alum is added, the negative charges are neutralized and a mutual attraction results. Keaton²² mentions the possibility of manufacturing pigment colors which have a direct affinity for cellulose fibers.

Effect of Order of Addition

Pigments may be added either before or after the size, but the alum should not be added until the pigment is thoroughly mixed with the fiber. Beating has a very pronounced effect on the results obtained with pigments, since a well-beaten stock retains more pigment than a lightly beaten one (see Chap. IX). It is generally advisable to beat the pulp for thirty to ninety minutes after the addition of the pigment and alum in order to develop the full strength of the pigment.

In spite of the best precautions that can be taken, pigments usually produce extremely two-sided papers as a result of a greater concentration of pigment on the felt side of the sheet. This is the result of the weak bond which is normally produced between the pigment particles and the fibers and is intensified on high-speed paper machines.

²⁰ J. Keaton, *Paper-Maker* 95, No. 4: TS 57-64 (Apr., 1938)

²¹ J. Keaton, *Paper-Maker* 95, No. 4: TS 57-64 (Apr., 1938)

²² J. Keaton, *Paper-Maker* 95, No. 4: TS 57-64 (Apr., 1938)

It is practically impossible to grind a pigment small enough that it can penetrate into the pores of cellulose fibers, and for this reason, all pigments, if they become attached to the fiber at all, must become attached to the outside of the fiber. The textile chemist surmounts this difficulty in several ways. One process, utilized in textile coloring, is to form an insoluble dyestuff *in situ* by reacting two soluble components after they have diffused into the pores of the fiber. A precipitate of the pigment results, but it will tend to wash out of the fiber, unless it has an affinity for the cellulose or unless its particle size is so large that it cannot pass through the pores. As recently as ten years ago, lead chromates, insoluble Prussian blue, and iron blacks were produced directly in the beater by a similar procedure.

Special Coloring Processes

Within recent years there has been an increasing demand for colored papers of improved fastness to light and water. Papers for automobile seat covers, paper rugs, other twisting papers, colored papers for use in plastics, etc., are some examples of papers which must meet rigid specifications.

In the past, pigments were used exclusively for the coloring of the above papers, but in many ways pigments have proved unsatisfactory. Very few of the soluble dyestuffs belonging to the conventional classes of acid, basic, and direct dyestuffs have the necessary requirements. Of these, the direct dyestuffs have the greatest natural affinity for cellulose and hence the greatest fastness to water, but they are always soluble in water to some extent, and this solubility accounts for their being less than 100% water-fast. Some of the basic or acid dyes also make fairly water-fast dyes, particularly where they are fixed on the fibers by mordants, but the limitations of these conventional coloring processes have led the paper chemist to look for more satisfactory coloring agents.

Recently the paper chemist has shown considerable interest in special coloring processes used by the textile industry in which soluble dyes are applied to the fiber and then fixed on the fiber by indirect methods which convert the soluble dyestuff into an insoluble form. These dyestuffs may be converted into an insoluble form by treatments with diazotization agents or with copper sulfate or formaldehyde. Some of these special coloring processes which appear to be most practical for application to papermaking processes are discussed in the next part of this chapter.

Coloring with Sulfur Colors

Sulfur colors are widely used in the dyeing of cotton for textiles, although they have never been widely used for the coloring of paper. The

dyestuff itself is insoluble in water, but can be converted into a soluble form by reduction with sodium sulfide solution. The soluble reduced dye has a strong affinity for cellulose fibers and becomes strongly attached to the fibers. Upon oxidation with air or oxidizing agents, the dyestuff reverts to its original insoluble state, resulting in colored fibers which retain their color even upon washing in water. Sulfur dyestuffs have one disadvantage in that they tend to produce dull shades.

When used for the coloring of paper, the sulfur color is reduced by sodium sulfide and dissolved in hot water (in which it is readily soluble in its reduced state), and then is added to the beater. As a precaution, a small amount of sodium sulfide may be added to the stock in the beater in order to destroy any oxidizing agents which might be present, such as might be left over from the bleaching process. Upon addition to the beater, the reduced color exhausts rapidly on the fiber. Oxidation by air then gradually causes the dye to develop its original color and revert to its original insoluble form. About 50 to 100 lb. of sodium chloride may be added to aid in exhausting of the color on the fiber, and the beater should be heated to 120° F. in the same manner as for direct dyestuffs. Sometimes heavy metal salts such as zinc chloride are used to eliminate the fumes of hydrogen sulfide which are liberated from the sodium sulfide. In some cases, copper sulfate is used for this purpose, but copper sulfate is not recommended, since it tends to form free sulfuric acid which reduces the strength of the paper. Lips²³ recommends approximately 1.5 lb. of zinc chloride for each pound of sodium sulfide which is added to the beater. The zinc chloride should be added before the size or the alum. In addition to removing fumes of hydrogen sulfide, heavy metal salts precipitate the excess sodium sulfide as a heavy metal sulfide and also neutralize the alkalinity. When properly used, sulfur colors are completely exhausted on the fiber and the backwater will be clear.

Naphthanil Coloring Process

The naphthanils belong to a class of textile dyestuffs called azoic colors, which are formed by the coupling of two dye intermediates on the fiber to form an insoluble color directly on the fiber. The naphthanil colors are bright, fast to water, and also fast to light.

So far, the naphthanil coloring process has not been used to any great extent in the paper industry, but Lips²⁴ has described the preparation of naphthanil dyes for use in the coloring of paper. The process must be carried out in two stages: First, the naphthanil or coupling component must be mixed in alcohol and sodium hydroxide solution to form the sol-

²³ H. A. Lips, *Paper Trade J.* 118, No. 13: 105-108 (Mar. 30, 1944)

²⁴ H. A. Lips, *Paper Trade J.* 118, No. 13: 105-108 (Mar. 30, 1944)

uble salt; next, a solution of the diazo or developing component must be prepared by either diazotization of the free base (reacting with acid and sodium nitrite) or by simply dissolving an already prepared stabilized diazo salt which can be purchased. In beater coloring, the former component, called the prepare, is added first and allowed to exhaust on the fiber before the diazo is added, with salt being added after the prepare in some cases to assist in exhausting it on the fiber. When the diazo is added, coupling takes place almost immediately with the formation of color directly on the fiber. The beater should be slightly alkaline for best results, and size and alum help to increase the strength of dyeing.

In surface coloring, the prepare is applied first by means of a roll coater and allowed to penetrate into the sheet before a solution of the diazo is applied. Coupling takes place almost immediately upon application of the diazo. The diazo solution may contain acid to neutralize the alkali added in the first bath.

Vat Colors

Vat colors are used in the textile industry for dyeing "color fast" fabrics and recently have been used to some extent for the coloring of paper. The process is very similar to that used with sulfur colors in that the dye-stuff itself is water-insoluble and must be reduced to a soluble state before application. One of the differences between the two processes is that sodium hydrosulfite is used to reduce vat colors instead of the sulfide used with sulfur colors.

In beater dyeing with vat colors, the following procedure is used. The vat color in the form of a water-dispersible powder or paste is added to the beater and a calculated amount of caustic soda added. Sufficient time should be allowed for the color to become uniformly distributed throughout the beater, after which the beater should be heated to 120 to 140° F. The vat color, which is still in the form of a water-insoluble pigment, is then temporarily solubilized by the use of a reducing agent. Sodium hydrosulfite is the most effective reducing agent, and the required amount is added dry to the beater. In this soluble, or "leuco," form, the dye has a pronounced affinity for the fiber and will exhaust readily. The reduced form of the vat dye is not stable and will readily reoxidize to the original vat dye, either by air oxidization or, if necessary, the rate of oxidation can be increased by adding cold water or an oxidizing agent such as sodium perborate to the beater. After the color has reoxidized, the beater should be neutralized with alum or a weak acid. The paper may then be sized in regular fashion.

Paper may be dyed in the above manner to cover a whole range of shades. The colored paper is fast to light, fast to water bleeding, and is non-two-sided.

Factors Affecting Coloring

Dyestuffs are extremely sensitive chemical compounds, and almost anything added to the stock will affect the results. Because of this sensitivity, the beater furnish should be exactly the same each time a formula is run in order to obtain the same color from the dyestuff. It is also important to maintain the same order of addition each time. In most cases, the dyestuff should be added before the rosin and alum, except when it is desirable to retard the absorption of dye by the fiber, in which case it is sometimes advisable to add the dyestuff after the rosin. It is generally best to add the dyestuff as early as possible in the furnishing of the beater to give it the maximum time to be adsorbed by the fiber. Stainless steel or glass-lined equipment is best for dissolving color. Wood barrels have the disadvantage of soaking up color and being difficult to clean.

Effect of Beating

Every papermaker knows that increased beating deepens the shade of colored papers. In early days, chemists attributed this phenomenon to an increased adsorption of dyestuff by the beaten pulp. In fact, they were so convinced of this fact that some early workers proposed the use of certain dyes, such as Congo red, for measuring the amount of fiber surface created during the beating process. Such a conclusion was not unwarranted at the time, since a similar test was being used in the textile industry to measure the degree of mercerization of cotton fiber, but subsequent work has shown that the same conditions do not prevail in the case of beaten fibers.

When a dyestuff is added to the beater and samples of stock for making into handsheets removed at regular intervals during the beating process, the color of the handsheets gradually increases in intensity as beating continues, until at maximum beating a very intense shade is produced.²⁵ In general, a glassine sheet will have about twice the depth of shade as a sheet of low density. Since the same amount of dyestuff is present in the beater in both cases, the increase in depth of shade must be attributed to one or both of two causes: (1) that more dyestuff is adsorbed by the fibers or (2) that there is a difference in physical properties of the papers which affects the intensity of color. Kress and Bialkowsky²⁶ proved that the latter was the case, in contrast to what paper chemists had long thought. Their work proved that beating does not appreciably increase the adsorption of soluble dyestuffs, and that the increase in color intensity obtained on highly beaten pulp is due to the more dense and compact character of the sheet, and not to a difference in dye adsorption. The

²⁵ O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 219-228 (Nov. 12, 1931)

²⁶ O. Kress and H. Bialkowsky, *Paper Trade J.* 93, No. 20: 219-228 (Nov. 12, 1931)

effect can be explained by the fact that beating decreases the number of air-cellulose interfaces in the sheet, and hence decreases the amount of reflected light and increases the amount of transmitted light. Since the amount of transmitted light is increased, there is greater opportunity for the dyestuff in the sheet to absorb light of specific wavelength and thus increase the proportion of "colored" light. Calendering has the same effect, to a lesser extent, and may increase the depth of shade by as much as 10 to 15%.²⁷ A similar effect can be demonstrated by taking a piece of colored paper and waxing it. The waxed paper will appear twice as strong in shade as the unwaxed paper.

Although the principal effect of beating it to change the amount of absorbed light, it is possible that beating may also have a slight effect on the retention of dyestuffs. Sears²⁸ found in his experiments with the electron microscope that dyestuff particles appear to be concentrated in the most fibrillated section of the fiber.

The amount of beating is an important factor when pigments are used, and it is necessary to maintain a strict beating schedule in order to obtain the desired shade from most pigments. The commercial pigments sold today are, for the most part, well dispersed and develop full strength in the beater very quickly, but some, such as carbon black, and the earth pigments, such as ochre and umber, tend to break down into smaller particles on prolonged beating, and care should be taken with these pigments to use the same amount of beating each time, and also give them the maximum amount of beating possible. A slow rate of color development in the beater is characteristic of a few dyestuffs, e.g., nigrosine and the anthraquinone blues.

Coloring Different Pulps

The results of coloring are dependent upon the type of pulp which is used, since pulps vary in their attraction for different dyestuffs. The coloring of mixed furnishes always presents a difficult problem, particularly when a combination of bleached and unbleached pulps is used. An example of a particularly difficult mixed furnish is that of bleached soda pulp, which has practically no affinity for basic dyestuffs, and groundwood fibers, which are readily dyed with basic dyestuffs. The same situation exists in the coloring of mixed furnishes of bleached sulfite and groundwood, since the groundwood pulp has a much greater attraction for basic dyes than the sulfite pulp. When basic dyes are used for coloring mixed furnishes, the result is usually a mottled effect in the finished paper. Thus, it is generally advisable to use acid dyes for coloring furnishes such as these. Many of the

²⁷ L. C. Lewis, *Paper Trade J.* 103, No. 22: 323-330 (Nov. 26, 1936)

²⁸ G. R. Sears and E. A. Kregel, *Paper Trade J.* 114, No. 12: 139-145 (Mar. 19, 1942)

difficulties have already been discussed and procedures given for their correction.

Although mixed furnishes present the greatest problems in coloring, there are plenty of difficulties in coloring relatively pure furnishes. Groundwood is often difficult to dye uniformly because of its non-uniform chemical and physical properties. One of the most difficult problems is to obtain uniform penetration of dyestuff into bundles of groundwood fibers which are firmly held together, and usually quite impervious because of their resin content. Kraft pulps present coloring problems because of the naturally reddish color which is difficult to offset. Pulps from certain species of wood present more difficult coloring problems than others, due to the presence of specific chemicals in some of the fibers or to an unusual morphological structure. For example, poplar pulp does not take dyestuffs as uniformly as spruce pulp. Bleached sulfate pulp made from southern pines dyes differently than pulp made from spruce, particularly when basic dyes are used.

The brightness of the pulp is a very important factor in coloring. In cases where regular orders of colored paper are run at different times, it is necessary to control the brightness of the pulp if uniform dying is to be realized. Slight variations in brightness will be quite noticeable when light shades, tinted white, or exceptionally bright shades are desired. If a bright, colored paper is desired, it is essential to start with a pulp of high brightness.

Effect of Sizing

The rosin and alum used in sizing of paper have a major effect on the coloring process. The effect which rosin has in retarding the adsorption of dyestuff when added before the dyestuff has already been mentioned. In other cases, the rosin acts as a mordant. Precipitated alumina undoubtedly plays an important role in the coloring of paper because it has a strong attraction for many dyestuffs²⁹ and probably acts as a mordant. It also affects light fastness and in general, the greater the amount of alumina present, the poorer the light fastness.

Some papers must of necessity be made without sizing agents. These are principally blotting papers, absorbant tissues, and papers for impregnation. Because these papers contain no size to act as a mordant, it is desirable to use colors which have some natural affinity for the cellulose. Direct dyestuffs are used, together with salt and high temperature, to aid in setting the color. In some cases, basic dyestuffs and pigments may be used with a small amount of alum.

Wet strength resins have been used in the textile industry for many

²⁹ L. Friedman and D. V. Kuykendall, *Paper Trade J.* 99, No. 12: 147-148 (Sept. 20, 1934)

years and have been found to improve the water fastness of the colored fabric, on account of reaction between the resin and the dyestuff which forms a complex salt of diminished solubility.³⁰ Lips³¹ noted in the dyeing of paper that wet strength resins increased the color retention and water fastness and, with certain colors, increased the light fastness, but decreased the light fastness of other colors. He also noted that the presence of wet-strength resins caused most paper to run two-sided.

Effect of Fillers

Many of the common fillers used in the loading of paper have a pronounced affinity for dyestuffs. Some fillers absorb approximately the same quantity of color as the paper fiber,³² and some fillers have greater adsorption for dyestuffs than the fiber.³³ Even inert fillers have a strong adsorption for direct dyestuffs, even though they have little affinity for acid or basic dyes.

Certain clays adsorb all types of dyestuffs, whereas other clays have no adsorptive capacity for acid and direct dyes.³⁴ The ratio of alumina to silica, the particle size, hydration capacity, and presence of impurities are some of the properties of clays which have an important influence on the adsorptive capacity for dyestuffs. Other pigments aside from clay adsorb dyestuffs. Diatomaceous earths have an affinity for basic dyestuffs, but not for acid dyestuffs.³⁵ Alumina has a strong affinity for most dyestuffs.³⁶ Titanium dioxide has a great effect on dyestuffs, and Lips³⁷ reports that the use of 4% titanium dioxide in the fiber furnish will mean that almost 50 to 100% more dye will be needed to maintain the same color depth as in paper with no titanium dioxide. China clay has an even greater adsorption than titanium for certain dyes, for example, methylene blue.³⁸

Because fillers tend to rob the fiber of dye, the color of filled paper is generally weaker than it would be if no filler were present. Naturally, fillers with the greatest adsorptive power lower the color to the greatest extent. Thus, it is desirable to use fillers with minimum adsorptive powers, and to follow an order of furnishing which reduces the effect of the filler. One method or minimizing the effects of adsorption is to add the filler last, as

³⁰ *Textile Weekly* 29: 563-564 (1942)

³¹ H. A. Lips, *Paper Mill News* 68, No. 41: 14-18 (Oct. 13, 1945)

³² F. A. Soderberg, *Paper Trade J.* 97, No. 21: 251-252 (Nov. 23, 1933)

³³ L. Friedman and D. V. Kuykendall, *Paper Trade J.* 99, No. 12: 147-148 (Sept. 20, 1934)

³⁴ O. Kress and P. Trucano, *Paper Trade J.* 117, No. 10: 109-116 (Sept. 2, 1943)

³⁵ O. Kress and P. Trucano, *Paper Trade J.* 117, No. 10: 109-116 (Sept. 2, 1943)

³⁶ L. Friedman and D. V. Kuykendall, *Paper Trade J.* 99, No. 12: 147-148 (Sept. 20, 1934)

³⁷ H. A. Lips, *Tappi* 33, No. 11: 106A-108A (Nov., 1950)

³⁸ L. Friedman and D. V. Kuykendall, *Paper Trade J.* 99, No. 12: 147-148 (Sept. 20, 1934)

close to sheet formation as possible. Thus, by adding the dye first and fixing it upon the fiber with rosin and alum before the filler is added, there is less tendency for the filler to rob the fiber of color. On the other hand, some papermakers prefer to make a paste of the filler and color and add the mixture to the beater, particularly when certain basic dyes are used, because they feel that this results in more even coloring.

Fillers are sometimes responsible for color two-sidedness in paper because of their preferential adsorption of the dyes. For example, certain acid dyestuffs have a strong affinity for the fiber but little affinity for the filler and consequently color the wire side of the paper deeper than the top side, because the uncolored pigment is sucked from the bottom of the sheet, thereby leaving a higher proportion of colored fiber on that side. When this trouble occurs with clay-filled papers, Lips and Roberts³⁹ suggest the use of a small portion of dyestuff, e.g., one of the stilbene yellows, which has more affinity for the clay than for the fiber and will balance the color on both sides of the sheet. In other words, more clay appears on the topside of the sheet, and the clay being more heavily colored by the stilbene will tend to offset the more highly colored fiber on the underside of the sheet. Two-sidedness may also be balanced in this way by using two dyestuffs of similar shade, one of which has an affinity for the fiber and the other for the filler. Color two-sidedness is often a serious problem and is caused by other factors than the presence of filler. It is discussed at greater length in a later section.

Effect of Residual Chemicals

Highly acid or highly alkaline substances affect the shade of dyestuffs, since many of the common dyes are indicators and, as such, are sensitive to small changes in the pH of the system. Oxidizing and reducing agents are particularly harmful to dyestuffs. Residual chlorine or hypochlorite, which might be present in bleached stock, has a decidedly detrimental effect on dyestuffs, and consequently bleached stock should be well washed to remove all traces of these substances.

Starch has been known to affect the shade of colored papers. For example, oxidized starch, with its carboxyl groups, attracts basic dyestuffs more strongly than native corn starch or other types of modified starch, and there have been several cases where changing the type of starch added to the beater has affected the shade of the paper. Cases such as this are not difficult to control and, in fact, no trouble develops until the furnish is changed.

Calcium salts which may be present in hard waters are harmful to certain dyestuffs, particularly acid dyestuffs, which may be precipitated

³⁹ J. R. Roberts, *Paper Ind.* 24, No. 9: 941-943 (Dec., 1942)

from solution if the water is very hard. In such cases a small amount of alum is sometimes added to the beater before the dyestuff in order to reduce the hardness.

Effect of pH

The pH has an important effect in coloring. Roberts⁴⁰ stresses the importance of pH control in dyeing, but Chalon⁴¹ points out that it is more important to maintain the optimum pH for filler and size retention than to maintain the optimum pH for coloring. However, it is vitally important to maintain the pH of the beater and white water within certain prescribed limits at all times, since variations in pH will result in a variation in shade and depth of color from one order to the next. Many dyestuffs are changed greatly in shade by variations in pH, and there is at least one pigment, ultramarine, which is faded in too acid a medium. When dyeing with such important paper colors as Congo red and benzopurpurine, pH is particularly important. These dyes are actually indicators, and in order to obtain the desired bright shade, they should be dyed at a pH around 6.0–6.5. The fastness of dyes to light is generally best when the pH of the paper is near neutrality.

There is an optimum pH for the retention of each color, and whenever possible, it is desirable to maintain the pH at this point. However, if the pH of optimum retention is going to affect drastically the shade of the color, some sacrifice of retention will have to be made. For most colors, the optimum retention is obtained within the pH range of 4.5 to 5.5, but there are some exceptions, e.g., methylene blue at pH 6.5. Acid dyestuffs are affected most by pH, and their retention decreases rapidly above a pH of 5.0.⁴² Direct dyestuffs are affected least by pH.

Two-Sidedness in Coloring

In addition to structural two-sidedness, there is another cause of two-sided appearance in paper and that is color two-sidedness. The latter is often related to structural two-sidedness because the characteristics of the sheet surfaces may be such that light is reflected differently on the two sides of the sheet, giving the appearance of different color, even though the fibers may actually be colored the same on both surfaces. In many cases, however, the effect is due specifically to color two-sidedness or, in other words, the different appearance is due to a greater concentration of color on one side of the sheet than on the other. This difference results from the greater affinity of the dye for the fines in the sheet and the greater concentration of these more highly dyed fines on the felt side.

⁴⁰ J. R. Roberts, *Paper Ind.* 15, No. 6: 313–315 (Sept., 1933)

⁴¹ O. T. Chalon, *Paper Trade J.* 104, No. 1: 26 (Jan. 7, 1937)

⁴² W. D. Harrison, *Paper Trade J.* 105, No. 13: 179–185 (Sept. 23, 1937)

Many factors may be responsible for two-sidedness. The use of suction couch rolls, suction boxes, and suction press rolls has increased the tendency toward color two-sidedness, because these increase the amount of structural two-sidedness of the paper. The problem of two-sidedness has become more acute during recent years, due to increased speeds of the paper machine. The action of the table rolls in removing fines from the underside of the sheet is an important factor in two-sidedness. In the case of one mill experiencing marked two-sidedness, it was found that the two-sidedness was as pronounced in samples of the paper taken halfway down the wire as it was in the finished paper, indicating that the initial loss of coloring matter was probably the predominating factor.⁴³ As a rule, when two-sidedness is present, the backwaters will be highly colored and the stock from the save-all will be more highly colored than the beater stock because of the greater percentage of highly colored pigment and fines which are present.

The effect of fillers on two-sidedness has already been discussed in a preceding section. Starches have been known to cause two-sidedness because of their greater attraction for certain dyestuffs and their tendency to concentrate on the surface. As already mentioned, fines may be the cause of color two-sidedness because of their preferential attraction for certain dyestuffs and their tendency to concentrate on the felt side. Most dyestuffs seem to have greater affinity for fines than for the long-fibered stock, probably because of the higher content of pitch, resin, lignin, and degraded cellulose products in the fines.⁴⁴

Certain dyestuffs have a more pronounced tendency toward two-sidedness than others. There are some dyestuffs which almost always cause marked two-sidedness, and others which almost never do. The reasons for these differences in behavior are obscure, but the dyestuffs which are most likely to produce two-sidedness are those which have a special affinity for certain fractions of the stock, such as fillers, sizing agents, fines, and starches, which tend to concentrate on one side of the sheet. Dyestuffs cannot be divided into those which cause marked two-sidedness and those which do not on the basis of type of dye alone. In general, direct dyestuffs as a class would be expected to show a minimum of two-sidedness because they have a marked affinity for cellulose, but there are many direct dyes which exhibit two-sidedness. Acid dyestuffs frequently show two-sidedness, since they have a greater affinity for the fines in a pulp, due to the high lignin content of this fraction. Basic dyestuffs also have a greater affinity for the fines than for the longer fibers, and thus tend to cause two-

⁴³ J. R. Roberts, *Paper Trade J.* 81, No. 14: 131-132 (Oct. 11, 1925)

⁴⁴ O. Kress and E. J. Loutzenheiser, *Paper Trade J.* 114, No. 11: 133-136 (Mar. 12, 1942)

sidedness. However, basic dyes show little tendency toward two-sidedness when used in unbleached sulfite. In some cases, a small amount of organic dispersing agent will reduce two-sidedness, presumably by reducing the affinity of the dye for the fines.

According to Lips,⁴⁵ there are only three dyes which will produce a truly non-two-sided sheet from unfilled stock on modern high-speed paper machines, and these are:

- (1) Brilliant crocein (a red), an acid dye.
- (2) Ruby PL (a red), an acid dye.
- (3) Brilliant paper yellow (a yellow), a direct dye.

A few additional dyes may be classified as fair, in that they are entirely satisfactory for slow machines, but are not satisfactory for high-speed machines. These dyes are as follows:

- (1) Quinoline yellow (a yellow), an acid dye.
- (2) Quinoline yellow P (a yellow), a direct dyeing acid dye.
- (3) Yellow S X G (a yellow), a direct dye.
- (4) Anthroquinone blue types (a blue), acid colors.
- (5) Red 8BLX (a red), a direct dye.

Since most of the other acid and direct dyes show severe two-sidedness, nearly all the bond shades are being dyed with the above dyes.

Colored pigments are notorious in their tendency to exhibit two-sidedness. The pigment invariably stays on the top of the sheet, leaving the bottom side a much lighter shade. Some attempts have been made to correct two-sidedness by tinting the wire side of the sheet in the press section, or at the size press, but this approach has not been very successful because of the mechanical difficulties involved. Mixtures of a pigment and a soluble dyestuff in the same paper may result in a two-sided effect in which there is a marked difference in color between the two sides of the paper. For example, using a mixture of Prussian blue (a pigment) and fast yellow (a dyestuff) to produce a green paper will likely result in a blue-green color on the felt side and a yellow-green color on the wire side.^{45a}

One cause of two-sidedness that should be mentioned is the tendency of some colors to "burn" on the drier. A hot drier will cause acid and some direct colors to migrate to the upper surface of the paper, resulting in a two-sided appearance commonly referred to as "burning." Two-sidedness can sometimes be minimized by having the hot driers strike the top side of the sheet first to drive part of the color to the more weakly colored under side of the sheet.

⁴⁵ H. A. Lips, private communication to the author

^{45a} F. A. Craig, *Paper-Maker* Midsummer No.: 14-25 (1950)

Coloring of Mottled Papers

Mottling is sometimes intentionally induced on certain grades of paper, as for example, some grades of cover papers, stationery, blotting papers, safety papers, and wall papers. Mottled papers, sometimes called granite or silurian papers, are prepared by adding a small quantity of highly colored fiber to a large quantity of white or other lightly colored stock. Although not widely produced, mottled papers are interesting for the reactions that are involved.

Preparation of Mottling Fiber

In preparing the colored fiber for mottled papers, unbleached sulfite, bleached sulfate, jute, or cotton rag fiber may be used, rag fiber being preferred because of its greater fiber length. Mottling fibers are not beaten any more than is necessary, since it is desired to keep them long in order that that may show up prominently in the finished sheet.

Either basic or direct dyes may be used for preparing the mottling fibers, but direct dyes are best because they have the greatest affinity for cellulose and consequently do not "bleed" or wash out and color the rest of the paper. In preparing the colored fiber, the dye, equivalent to about 2% on the weight of the fiber, is dissolved in a small quantity of hot water and then added to the pulp which has been thoroughly broken up. More water is added until the dye solution just covers the pulp, after which about 10% of common salt (NaCl) or 20% of Glauber's salt (Na_2SO_4) is added and the suspension heated to 90 to 95° C. and held for about thirty minutes with frequent stirring. The suspension is then allowed to cool, 2% alum on the weight of pulp is added, and the mixture is agitated for about fifteen minutes. Next, the fibers are filtered and washed until the wash waters are absolutely colorless. This may require several hours and the use of large volumes of water. The fibers are drained thoroughly after washing, since this helps to prevent bleeding. Sulfur colors are also used for dyeing mottling fibers. In some safety papers, fluorescent dyes or special chemicals are used for treating the mottling fibers.

Preparation of Mottled Sheet

The mottled sheet is prepared by adding a small quantity of the deeply dyed fibers, usually from 0.5 to 5.0% of the total fiber furnish, to a white or lightly colored pulp stock, which forms the main background of the sheet. The pulp used for the background, which may be bleached sulfite, rag, or similar stock, should be thoroughly beaten and sized before the addition of the mottling fibers. If the background is colored, it should be dyed before the addition of the mottling fibers. After the mottling fiber has been uniformly mixed with the background stock, the mixture is ready to be formed into paper.

Calender Coloring

In addition to beater coloring, there is another type of coloring, called calender coloring. This method of coloring, which is used principally for the coloring of paperboards or heavy papers, involves the application of a solution of dyestuff to the surface of the paper at the water boxes of the calender stack. When acid dyes are used, a 1% solution may be used for light to medium staining, and a 2% solution for heavy staining. When basic dyes are used, a $\frac{1}{2}$ % dye solution is generally used. A similar application of color is also done at the size press.

Calender coloring is primarily a surface staining of the paper, although wetting agents may be used to increase penetration of the color into the paper. The solution of dye may be a simple water solution or an alcohol-water solution. Methanol is sometimes used as solvent for basic dyestuffs in calender coloring, but it is also a solvent for rosin and should be used with caution, since it may ruin the sizing in the sheet. It also presents a fire hazard.

If ordinary solutions in water are used, the colored paper will likely bleed when wet, although certain basic dyes become strongly fixed on unbleached pulps. Acid dyestuffs are frequently used for calender coloring because of their good solubility and uniform dyeing properties, but if the paper becomes wet during use, the color bleeds because of its high solubility and poor affinity for the cellulose. Basic dyes are used on cheaper grades where brilliancy is desired. Direct dyes are seldom used for calender coloring. If a binder is used with the color, the tendency toward "bleeding" is considerably reduced, particularly if the binder is water-resistant. Among the binders which are used are starch, casein, and sodium silicate. These agents are mixed in water according to normal procedure, the dye added, and the mixture adjusted with water to produce a colored solution of the proper viscosity. Casein makes an excellent water-resistant binder when the colored paper is given an after-treatment with a solution containing about 5% formalin and 18% alum.

Calender staining sometimes results in uneven dyeing because of unevenness in the sizing of the board. Surface-active substances may be of some value in surface staining by increasing the wetting of the paper and promoting swelling of the fibers. Sulfonated castor oil or ordinary soap is sometimes used in calender coloring with acid dyes to improve the evenness of dye absorption, but with certain basic dyes, soap results in precipitation.

Conversion Coloring

In the preceding section on coloring, beater dyeing and calender staining have been discussed. Both of these methods of coloring are done on the paper machine as the paper is being made. There are additional dyeing

procedures which are carried out as separate converting operations. The two most important are dip dyeing and aniline staining.

Dip Dyeing of Paper

The dip dyeing process for coloring paper is used for coloring creped decorative tissues and other light-weight papers. In this process, light-weight tissue paper is dipped in a strong dyestuff solution, the excess color is removed by light pressure between squeeze rolls or by a doctor, and the paper is then dried on a large drier roll where it is creped by a doctor knife as it leaves the drier and is wound on the reel.

In making up the color solution, the dye is generally dissolved in hot water and filtered before adding to the color pan. The dye bath is generally located directly under the driers so that the temperature of the dye bath will remain between 140 and 160° F., due to the heat from the driers. This high temperature is desirable to assist in obtaining maximum solubility of the dye.

Most shades dyed by this technique are bright and deep. It is therefore essential to use tinctorially strong dyes or dyes having excellent solubility. The highly soluble acid dyes are particularly good for this purpose, and solutions containing 2 to 6% acid dye may be used. Basic dyes may be used in some cases, particularly where maximum brilliance and low cost are desired. It is common practice to add animal glue or some similar product to the dye bath to assist in creping and holding the crepe in the finished sheet.

Aniline Staining

Frequently a paper consumer is interested in obtaining a wide range of shades on heavy-weight boards when his requirements are too small to warrant paper machine runs in the range of shades desired. In order to satisfy this need, a number of machinery manufacturers have built aniline-staining machines suitable for the surface staining of paper and paperboard in a conversion operation.

In this operation, acid, basic, and direct dyes may be used. In most cases the machines are not equipped with drying facilities, and it is therefore common practice to apply the dye from an alcohol or alcohol-water solution so that the paper will dry rapidly by evaporation of solvent. Equal parts alcohol and water, or a mixture of two-thirds alcohol and one-third water, are generally used.

Brilliance of color and economy are primary considerations in this process. It is also necessary to select dyes that are soluble in alcohol or alcohol-water solutions. The dyes which most nearly satisfy these requirements are the basic dyes, and all the basic dyes are satisfactory, with the exception of methylene blue, which is practically insoluble in alcohol.

When basic dyes are applied from alcohol-water solution to unbleached papers or paperboards, the color is practically waterbleed-fast, although there is considerable bleeding when applied to bleached papers.

In some cases it is desirable to surface-dye bleached papers. Acid and basic dyes may be used for this purpose as described above, but the product will not be fast to water. If waterbleed fastness is a requirement, it is necessary to use special spirit-soluble color lakes dissolved in alcohol or in an alcoholic-water mixture. Spirit-soluble lakes of basic dyes such as the tannic acid lakes are sold by all the dyestuffs manufacturers. These are naturally much more expensive than the basic dye itself, but are required for use on bleached papers if waterbleed fastness is an important requirement.

Papers surface-stained by the above process are used extensively for colored suit boxes, decorative wrappings, fruit basket liners, etc. As can be seen, the operation is a simple one and may be used for all-over printing and also for design printing by proper manipulation of the color formula and the use of engraved rolls. The process is used mainly for all-over printing where the amount of paper involved does not justify a special mill run of colored paper. In this way, the converter stocks only one or two grades of uncolored paper, and then colors the board as required.

Color Matching

Color matching is the most important job of the colorist in the paper mill. This requires experience and a knowledge of the basic factors involved, the most important of which will be discussed. The physical measurement of color is discussed in the section on absorption of light in Chapter XVI.

In order to select the best colors for use in matching a particular shade, a good deal of practical experience is necessary. While skill in color matching can be acquired only by experience, there are a number of elementary principles which are helpful in selecting colors.

Method of Coloring

The method to be used for coloring a shade is often dictated by the equipment available at the mill. It has frequently been stated that 95% of all colored paper is dyed in the beater. Beater coloring is generally the logical choice and, for many grades of paper, the only choice. However, board mills frequently have the choice of beater dyeing, calender staining, or a combination of both, and in this type of mill, the question of method of coloring is very important. Each method has its own particular advantages and its own disadvantages, and these must be balanced against the requirements of the paper.

Beater dyeing is more expensive than surface staining. When shades

are changed in beater dyeing (particularly deep shades), a wash-up may be necessary to clean the system, which means a loss in time and some loss in stock. Calender coloring, on the other hand, is considerably cheaper because only the outer surface of the paper is stained. The heavier the paper, the greater the cost advantage in favor of calender coloring. Brighter shades can be produced by calender staining than by beater dyeing, and the shades produced by calender staining are faster to light. Calender-applied colors, however, will water spot, will generally bleed considerably when wet, and will wear under slight rubbing, thereby exposing the undyed base stock. These are some of the factors which must be balanced, one against the other, before deciding upon the method of coloring.

Primary Colors

The three primary colors of the dye chemist are red, yellow, and blue. By mixing these three primary colors in the proper proportions, it is possible to obtain a wide variety of shades. Each of the primary colors has its own peculiar attributes, and these may be expressed as follows:

- (1) Yellow is the brightening color and adds light to all colors and mixtures.
- (2) Red is the color of warmth and glow and warms all mixtures.
- (3) Blue is the color of coldness and cools all mixtures.

When matching a color, if the trial match is laid beside the sample and a difference in brightness is noted, it is easy to tell whether too much or too little yellow has been added. If the trial seems warmer than the sample, then too much red is present, whereas if the color is too cold, too much blue is present. Black darkens all colors and, in general, the effect is displeasing. There is a difference between darkening a color and deepening it. To deepen a color, its complementary color must be added. Thus, green deepens red, violet deepens yellow, and orange deepens blue.

Dye Selection

The dye manufacturers offer almost three hundred different dyes to the paper industry. This brings up the question of why so many different dyes are offered, since it is possible to obtain almost any color by mixing the three primary colors. The answer is that each dye has specific properties and dyeing characteristics that are advantageous in certain instances. The colorist should attempt to learn as much as possible about the properties of all the important commercial dyes, since often he can make decided savings to his mill by a proper selection of dyes.

Single dyestuffs are sometimes used in producing a colored paper, but the number of shades which can be produced by single colors are few compared with the number of shades which can be produced using combinations

of colors. Shades produced with single colors are easy to produce and possess great brilliance, but they are harsh to the eye and almost never produce the pleasing effect of color combinations. Combinations of two dyes are frequently used and produce rather soft-toned effects, but are still somewhat less pleasing than combinations of three colors. In special cases, as many as four colors may be used.

The brightest shades are produced by using the color which most closely approaches the desired shade, and then using a small amount of another dye to obtain the desired shade. Usually all shades can be matched with three dyes or less, and the dyer should always remember that the addition of each dye is a step toward darkness. The possible combinations are limitless, and only by practice is the color sense developed to the point where it is possible to foretell the shade which will be obtained by mixing different colors.

Color matching is complicated by the fact that commercial dyestuffs are never pure shades of red, yellow, or blue, but rather contain traces of one of the other shades. For instance, most blues contain a little yellow, causing a green tinge or a little red giving the dye a violet hue. The reds are almost invariably either scarlets containing a trace of yellow, or crimsons containing blue. The yellows often tend toward orange or occasionally show a trace of green, showing the effect of red and blue respectively. Thus, instead of being able to cover the whole range of shades with red, blue, and yellow dyes, it is necessary, in working with commercial dyes, to use mixed colors intermediate between the primary colors, such as orange (red plus yellow), green (blue plus yellow), and violet (blue plus red) to obtain desired effects. The addition of the third primary or "complementary" color to any of these intermediates tends to produce a gray when all three colors are perfectly balanced, or if one color or another predominates, it is grayed and softened by the presence of small quantities of the other two. This is illustrated in Figure XIII-1.

In using dye mixtures, the component parts of each dyestuff used must be studied and care must be taken to use the final color in such quantities so as to soften but not spoil the first shade. The important rule to remember is that red, blue, and yellow, when mixed in equal strength, make a neutral gray or black. Accordingly, any one of these colors will tend to gray or neutralize a mixture of the other two colors. Thus, red will form gray with green, blue will form gray with orange, and yellow will form gray with violet. For the same reason, if there is too much red in a dyeing, it can be killed by the addition of a little green, and vice versa. In the same connection, it is frequently found that certain combinations of color produce

clear shades, whereas other combinations produce muddy shades. This latter effect is caused by an undesirable combination of trace colors in commercial dyes. By way of example, consider the possibility of obtaining a scarlet (red and yellow) dyeing, using a crimson (red and blue) dye. A combination of a yellow dye with the crimson red would result in a "muddy" brown because of the red, blue, and yellow combination tending to gray the predominant red color. On the other hand, the use of a red-dish orange with the crimson dye would tend to produce the desired scarlet color because the yellow would kill the blue in the crimson, whereas the red in the orange dye would add to the red in the crimson, thereby producing a yellow shade of red, or scarlet.

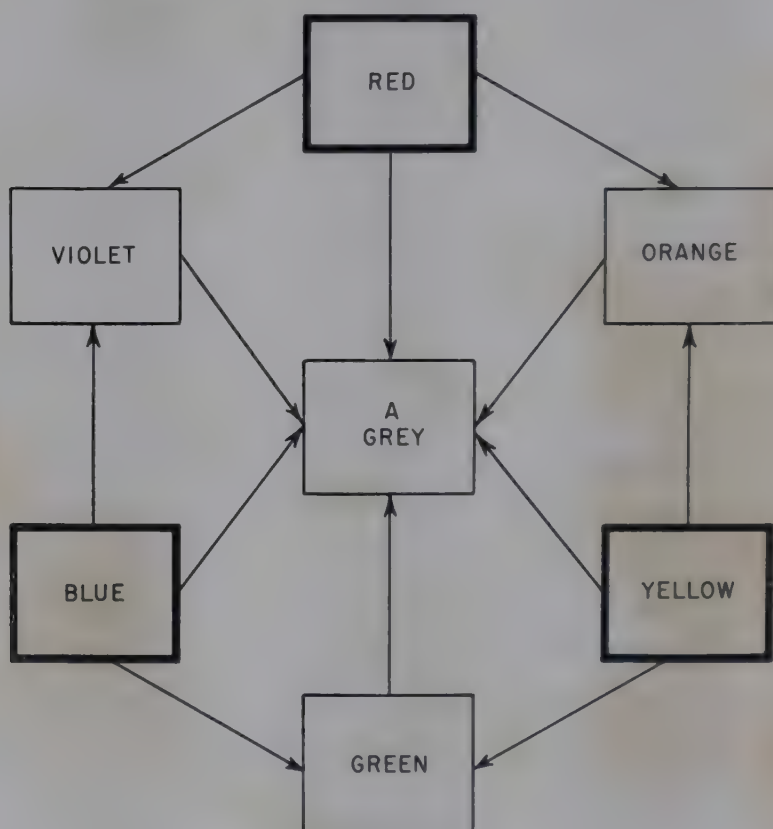


Fig. XIII•1. Color diagram.

Two-color shades

Red + Blue \rightarrow Violet
 Red + Yellow \rightarrow Orange
 Yellow + Blue \rightarrow Green

Complementary colors

Red + Blue + Yellow \rightarrow Gray
 Red + Green \rightarrow Gray
 Blue + Orange \rightarrow Gray
 Yellow + Violet \rightarrow Gray

The color of the pulp must be considered, since this affects the shade obtained with any dyestuff. For example, methylene blue produces a bright blue on bleached pulps, but gives a green-blue on unbleached sulfite and a deep olive green on unbleached sulfate.

In conclusion, it is helpful in choosing the proper dyestuff to have the following information on each dye considered:

- (1) Shade.
- (2) Dyeing characteristics on various pulps.
- (3) Light fastness.
- (4) Chemical fastness: (a) acid, (b) alkali, (c) chlorine (ink eradiator).
- (5) Solubility.
- (6) Tinctorial strength.
- (7) Price (particularly with the deeper shades).
- (8) Relative value ($\text{price} \times \text{tinctorial strength}$).

Importance of End Use

By knowing the properties of each of the important dyes, it is possible to balance the requirements of the paper with the properties and relative cost of the dyes and thus arrive at a desirable combination of colors for the shade in question. This cannot be done without knowing the following:

- (1) End use of paper.
- (2) Fastness tests required in paper: (a) light fastness, (b) chemical fastness.
- (3) Cost limitations.
- (4) Furnish to be used.
- (5) Fillers to be used.

In order to match a shade in a paper mill, it is desirable to have as much information as possible available about the paper, its requirements, and its end use. Only with this information will it be possible for the colorist properly to select the dyes for the particular shade in question. In matching a given shade, the color formula and the method of coloring should be selected to match the shade at the cheapest possible cost and the least loss of time, and still meet all the requirements dictated by the end use of the paper. In so far as possible, only dyestuffs having similar properties should be combined.

Frequently fastness tests are specified that greatly limit the color selection. These requirements are sometimes in excess of actual requirements, and careful thought regarding the end use of the paper will assist greatly in color selection. Typical examples of this are Christmas tissue, blue blotting paper, and goldenrod shades of bond. Christmas tissue is often dyed with benzopurpurine or Congo red, dyes which are cheap, but extremely sensitive to acids, and which will turn deep blue or black when spotted with acid. These dyes are used to advantage in this application, since the end use indicates that they will not come in contact with acids. Blue blotting is often dyed with Prussian or iron blue, which is a color that is destroyed by al-

kali, but again, alkali-sensitivity is of no importance in blotting paper. Goldenrod bond is sometimes dyed with brilliant paper yellow, a cheap, direct yellow, which is bright, fast to light, and generally non-two-sided, but which is extremely sensitive to alkali and turns a brilliant scarlet if the paper comes into contact with alkali. For bond papers, this dye is excellent, but on the other hand, it would be a poor dye to use for dyeing soap wrapper.

Laboratory Dyeings

Before undertaking a color match on the paper machine, it is desirable to have a laboratory match as a guide. All the dyestuff companies offer shade-matching services to their customers, and this service is often an extremely valuable guide in the mill. However, it is also desirable for the colorist to have laboratory facilities in his own mill so that he can make preliminary laboratory dyeings to serve as a guide during the mill run.

The only equipment required is an analytical balance to weigh small quantities of dye, a series of dye pots, six or more agitators, a sheet mold, and a sheet drier. Dyeings can be made on the basis of 3-g. sheets and 5-g. sheets and adjusted to match the shade.

When matching shades, the fiber composition of the sample to be matched must first be determined if it is not known, since each pulp has its own peculiar dyeing properties. The fiber composition is best determined by making a microscopical analysis of the paper. Once the proper furnish has been established, the same furnish should be used for both the mill and the laboratory runs. The stock should be beaten to the same extent in both cases, since the amount of beating affects the color of the paper. Finishing and moisture content for the sample to be matched and the handsheet should be the same. Highly finished papers (e.g., glassine) can be matched much better to the unsupercalendered sample. In matching water-finished papers, the sample may be steamed to remove the finish. With waxed papers, the sample for comparison should be dewaxed. Surface sizing alters the shade, and this should be taken into account when matching colors for paper to be surface-sized.

After the pulp has been properly prepared, the correct amount of pulp to give 3.0 g. of air-dry fiber is weighed out and placed in a color pot together with about 100 cc. of distilled water. The stirrer is then started in order to break up the fiber partially before adding the color. Unless otherwise stated, additions are made in the order of color, size, and alum. In adding the color, direct dyes should be added first, followed by the acid colors (light shades preceding dark shades). The basic colors are added last. After the color, the correct amounts of size and alum are then added, the size being added about five minutes after the color and the alum about

five minutes after the addition of size. Stirring is continued for a total time of thirty minutes. When stirring is complete, the pot is removed from the stirrer, filled three-quarters full of distilled water, and the sheets formed on a sheet machine. The sheets should be dried on a steam drier, care being exercised not to get the sheet too hot. The trial dyeing should be compared with the sample to be matched in the proper light, and dyeings repeated until a satisfactory match is obtained. The top side of the handsheet should be compared with the top side of the sample to be matched.

Very close approximations can be obtained by means of laboratory dyeings. The laboratory formula will rarely be perfect, but it serves as an excellent guide. In fact, it is not necessary to obtain a perfect match in the laboratory, and a reasonably close match with the color depth is often as good a lead as a perfect match. As a general rule, the laboratory formula requires 10 to 20% more color than will be required in the mill run (particularly with acid colors) because dyeing efficiency is better in the mill where the build-up in the return water contributes to the color strength. Therefore, in matching the shade in the mill, the laboratory formula should be cut 10 to 25%. It is always better to start on the weak side and build up with color, rather than start on the deep side and try to reduce the color depth. When making the final adjustments in color, it is desirable to obtain some wet-dyed pulp for the laboratory match and adjust the shade of the mill stock so that a wet sample will match the wet sample from the laboratory beater. This is of considerable help, and a close match of the wet samples will give reasonable assurance that the shade will match.

Making the Mill Match

The most important single point in regard to shade control is correct order of addition. The color should be added to the beater first before either the size or the alum. Many mills add the size first, and then the color, followed later by the alum. This procedure is satisfactory, but by adding the color first, more time is available for the color to dissolve and to become uniformly mixed in the beater. The important fact is to always add the color before the alum.

When trying to match a new shade in the mill, only one or two beaters should be colored at the start, leaving a few uncolored or lightly colored beaters, so that shade adjustments can be made rapidly. This is an excellent precaution and is helpful in cases where the first beater comes over the machine on the deep side. If this should happen, some uncolored or lightly colored stock may then be dropped into the chest to compensate for the excess color depth. When the backwater is highly colored, there will be a tendency for the shade to increase in depth in the early part of the run while the water works through the system.

Many dyes have a tendency to change shade after the sheet has passed over the driers, particularly acid dyes such as Metanil Yellow and Orange II. A sample fresh from the machine will frequently change shade for a period of five to ten minutes while the sheet is adjusting for humidity and temperature conditions. Thus, the sample should be cooled before judging. In some mills the shade is compared in north light during the daytime and under a standard daylight lamp during night shifts. Other mills standardize on a daylight lamp and match all shades under this lamp so that the light variations between shifts will be minimized.

Determination of Strength of Dyestuff

The determination of the strength of a dyestuff is an important determination where the color chemist finds it necessary to specify the dyes to be purchased by the mill. Dyestuffs vary greatly in strength, and this variation is not always offset by similar variations in prices. For this reason, a careful examination of the dyestuffs used in the mill is often a very profitable undertaking.

The comparison of two dyestuffs for strength may be made on a single pulp stock, such as unbleached sulfite, or on a mixture such as 50% unbleached sulfite and 50% groundwood. A moisture determination is first made on the pulp, and then an amount of wet pulp equivalent to 3.0 g. (air-dry) is used for each test.

The determination of the color value or strength of a dyestuff is made by arbitrarily adopting one dyestuff as a standard and comparing dyeings made from it with dyeings made from the dyestuff of unknown strength, all dyeings being made under the same conditions of concentration, temperature, etc. The dye being tested may prove to be either weaker or stronger than the standard dyestuff. Before actually making dyeings, pour-outs on filter paper can be made as a rough approximation. From the stains produced, the relative strengths of the dyes can be estimated. Closer estimates can be obtained by adding known quantities of distilled water to the stronger dye solution until its stain on filter paper is apparently equal to the color produced by the weaker dyestuff.

In making the final determination, the dyestuff solutions are made up in volumetric flasks of 1,000 cc. total volume. Then, 10 cc. of the standard dyestuff solution is added to a weighed amount of pulp in a dye cup. To the remainder of the cups, varying amounts of the unknown dyestuff solution are added. Then, size and alum (and any special fixing agents required) are added to all cups and hand sheets formed. The sheets dyed with the unknown dyestuff are compared with those of the standard dye, always matching the top side of the sheet. If an exact match is not obtained, the

procedure is repeated with different percentages of the unknown dye until a match is obtained. The relative strength of the unknown dye is determined by the amount required to match the dyestuff of known strength, and the results may be reported as the number of parts of unknown dyestuff equivalent to 100 parts of the standard dyestuff, or as a percentage of the strength of the standard dyestuff.

MICROBIOLOGY

Within recent years, microbiology has become an immensely important subject to the paper chemist. It is a relatively new field for him, and one which is related to many unfamiliar subjects, such as bacteriology, zymology, mycology, and enzymology. Bacteriology is the study of bacteria, mycology the study of molds, zymology the study of yeasts, and enzymology the study of enzymes. All these subjects are covered to some extent in this chapter under the inclusive term of microbiology.

Microorganisms are of importance to the paper chemist chiefly because of the troubles which they cause if they are not kept under control. Recent developments in the use of paper containers for milk and other food products, where highly sanitary conditions should be maintained, have brought the subject of paper mill microbiology to the attention of public health authorities. This has aroused interest in sanitation standards on paper packaging, and has led to the development of methods of testing to determine the suitability of certain paper products.¹ However, in addition to the factor of sanitation, microorganisms are important because of the troublesome conditions which they produce in mill systems, including slime formation, corrosion, decomposition and fermentation. These subjects will be discussed in detail in later sections of this chapter. It is sufficient to point out at this time a fact with which paper chemists have become increasingly familiar, namely, that excessive growth of microorganisms in a mill system invariably results in economic losses. By keeping these microorganisms under control, it is possible to effect savings through: (1) improvement in quality of the product, (2) reduction in number of rejects, (3) reduction in the economic loss of raw materials, (4) reduction in time losses, and (5) saving in felts and machine parts. These economic factors are important, even though no trouble with slime is experienced.

A large number of microorganisms, including bacteria, algae, yeast type fungi, and mold type fungi grow in paper mill systems. The paper chemist is interested primarily in killing or inhibiting the growth of these organisms. but before he can do this with any degree of success, he must understand their behavior. He should know the general types of organisms found in

¹ See TAPPI Standard Methods for Bacteriological Examination of Paper and Paperboard

paper mill systems, their habits of growth, and the effect of mill conditions on their development. It would be advantageous if he could identify the various genera and numerous species, but only the most highly trained microbiologist could be expected to do this. No attempt has been made in this book to instruct in the generic identification of microorganisms. The principal purpose is to acquaint the paper mill chemist with the importance of microorganisms in papermaking and to study methods for the control of these organisms.

It is realized that many paper mill chemists have little or no knowledge of microbiology, and this chapter has been written with that in mind. However, many of the large paper mills have one or more trained microbiologists on their laboratory staffs, and it is hoped that the material presented will be useful to them as well.

A great deal about the physical, chemical, and biological factors surrounding microorganisms is not completely understood. One reason for this is the difficulty in ascribing definite properties to a particular microorganism, since the properties vary according to the physical and chemical environment in which the microorganism is grown. However, many common types which grow in paper mill systems have been fairly well classified.

Types of Microorganisms

There are, in general, two principal divisions of microorganisms. These are the bacteria and the fungi. Bacteria are single-celled organisms which are usually spherical, rod-shaped, or spiral. The fungi are multi-celled organisms which grow in the form of filaments.

The flora of a paper mill system is diversified, and many groups of microorganisms can be found there at one time or another. Some of these are particularly troublesome, while others are not. Algae, fungi, and bacteria cause the greatest trouble. Other less harmful types which are sometimes present are the yeasts and protozoa.

All organisms are composed of vegetative cells, but some organisms form, in addition, specialized cells known as spores. Spores are produced abundantly by fungi at certain stages of their growth. Spores are also formed by certain large groups of bacteria. A bacterial spore is similar to a seed in higher plants. It is considered to be the dormant or resting stage of the organism. Spores have thick walls which permit them to withstand unfavorable conditions and, as a result, sporeforming bacteria can withstand extremes which would quickly destroy non-sporeforming species. For example, spores often survive the destructive effects of killing agents or heat and later germinate and grow when more favorable conditions are provided.

In the following sections, general information is given on the properties of algae, bacteria, and fungi.

Algae

Algae are plants which exist in the form of single cells or in groups of cells which adhere to one another to produce colonies or filaments. There are two general classes, called the green algae and the blue-green algae. Some algae are motile, that is, they can move about by means of cilia or long thread-like filaments which propel the organisms through the medium.

Since algae require air and water and thrive only in sunlight, they are found in the upper layers of aqueous media. For this reason, they are often present in outdoor water reservoirs where there is an abundance of light and air. They do not grow or reproduce to any extent in paper mill systems where conditions are not as favorable. Hence, algae are not so troublesome to the papermaker as bacteria or fungi, although there are times when they may interfere with normal operations. In these cases, the trouble is caused by conditions which originate in the water supply system.

Since most algae contain chlorophyll, they have the ability to absorb carbon dioxide and release free oxygen to the water supply. In this way they may increase the oxygen content of the water and thereby increase the corrosion of equipment when the water is used for cooling or other similar purposes.² Algae may cause trouble in the water treatment plant by interfering with the formation of alumina floc and lowering the efficiency of the coagulation and filtration steps in the water-treatment process.³ They may also cause trouble in the water-treatment plant by accumulating in the equipment and later breaking away in clumps to clog filters, screens, showers, etc. In some cases, they may impart tastes and odors to the water which are carried through to the finished paper. Since the organisms are colored, they tend to color the water and later cause discoloration of the pulp when the water is used for pulp washing.

Bacteria

Most bacteria exist as very small, single-celled plants which can be classified into three structural types: spherical (coccus), rod-shaped (bacterium or bacillus), and curved (vibrio). The bacteriologist recognizes the pathogenic or disease-producing types, and the non-pathogenic or non-disease-producing types. Paper mill bacteriologists are normally not concerned with the pathogenic types, since they are rarely found in paper mill systems.

There are three important groups of bacteria which should be recognized by the paper mill bacteriologist. These are: (1) the sporeforming

² R. B. Martin and J. G. Dobson, *Paper Trade J.* 121, No. 15: 143-150 (Oct. 15, 1945)

³ A. E. Griffin, *Paper Trade J.* 113, No. 9: 95-97 (Aug. 28, 1941)

bacteria, e.g., *Bacillus subtilis*, *Bacillus pumilus*, *Bacillus megatherium*, and *Bacillus cereus*; (2) the non-sporeforming bacteria, e.g., *Pseudomonas*, *Proteus*, *Achromobacter*, *Flavobacterium*, *Alcaligenes*, *Cellulomonas*, *Aerobacter*, and *Escherichia coli*; and (3) the filamentous or mold-like bacteria, e.g., *Actinomyces* and iron bacteria (*Crenothrix* or *Leptothrix*).

Bacteria multiply very rapidly under the right conditions. Some bacteria, known as aerobes, require oxygen, whereas others, known as anaerobes, grow only where there is little or no free oxygen. Still another group, called facultative, can grow with or without free oxygen. Most of the bacteria prefer a neutral or slightly alkaline medium. Bacteria cause considerable trouble in paper mills. Some cause slime, and others decompose cellu-



Fig. XIV-1. Colony of *Crenothrix polyspora* growing from a single point (180 \times).

lose. The filamentous iron bacteria (i.e., *Crenothrix* or *Leptothrix*) cause staining of the pulp by withdrawing iron from solution and precipitating it within their own structure as ferric hydroxide. A photomicrograph of *Crenothrix polyspora* is shown in Figure XIV-1. The filamentous bacteria sometimes attain lengths up to 200 microns, or even several millimeters, and have sheaths, swollen with ferric hydroxide, as thick as 2 to 8 microns.⁴

Microscopic Examination of Bacteria. Bacteria can be examined under a microscope at 950 \times using oil immersion. A slide can be prepared by transferring a small amount of the microorganism by means of a wire

⁴ K. Duchon and L. B. Miller, *Paper Trade J.* 126, No. 4: 37-48 (Jan. 22, 1948)

to sterile water on a glass slide. A cover glass is then applied and a drop of oil is placed on top of the cover glass. The oil immersion objective of the microscope is then submerged in the oil and the field is brought into focus.

Bacteria are near the limits of resolution of the ordinary microscope and are sometimes hard to distinguish. Filamentous types are sometimes mistaken for fibrillae.⁵ The rod-shaped bacteria ordinarily found in paper mill systems are about 0.5 to 0.8 micron in diameter and 1.0 to 2.0 microns in length. Others may be as large as 1.0 to 1.5 microns in diameter, and 3.0 to 6.0 microns in length.⁶ Appling and Shema⁷ have reported that one species of bacteria increased its normal cell size from a length of 2.0 microns to as much as 25.0 microns while becoming acclimatized to sodium pentachlorophenate in laboratory tests.

Gram Method of Staining. The bacteriologist makes use of many staining techniques for the classification and identification of bacteria. One of the most useful of these is the Gram method of staining for determining whether microorganisms are Gram-positive or Gram-negative. The value of this test is based upon the fact that in paper mill systems, about 90% of the time a Gram-positive organism is a sporeformer, whereas a Gram-negative organism is a non-sporeformer (notable exceptions are certain cocci).

The Gram staining method is carried out as follows:

- (1) A small amount of the microorganism is transferred to a clean glass slide and dried.
- (2) The dried organism is covered for 1 minute with a solution of crystal violet prepared by mixing solutions *A* and *B*.

Solution A

Crystal violet (90% dye)	2 g.
Ethyl alcohol (95%)	20 cc.

Solution B

Ammonium oxalate	0.8 g.
Water (distilled)	80 cc.

- (3) The crystal violet is washed off with tap water.
- (4) The organism is then covered for 1 minute with Lugol's iodine solution.

Iodine	1 g.
KI	2 g.
Water (distilled)	300 cc.
- (5) The slide is washed with water, blotted and dried, and then decolorized 30 seconds with 95% ethyl alcohol (agitating gently); then blotted dry.
- (6) The organism is then treated with safranin for 1 minute and washed with tap water, blotted and dried.

⁵ J. Strachan, *Paper-Maker* 111, No. 1: 1-2 (Jan., 1946)

⁶ R. B. Martin and J. G. Dobson, *Paper Trade J.* 121, No. 15: 143-150 (Oct. 15, 1945)

⁷ J. W. Appling and B. F. Shema, *Paper Trade J.* 117, No. 14: 157-160 (Sept. 30, 1943)

Safranin (2.5% solution) in 95% ethyl alcohol	10 cc.
Water (distilled)	100 cc.

After staining, the slide is examined under a microscope. If the cells are colored red, the bacteria is Gram-negative. If colored blue, it is Gram-positive.

Spore Stains for Bacteria. There are special stains for determining whether a bacterium is a sporeformer or a non-sporeformer, and these depend upon coloring the spore a different color from the rest of the organism. Malachite green and safranin are used in one method in which the Malachite green stains the spore green, whereas the rest of the cell is decolorized, and is then stained red with safranin.

One test is carried out as follows:

- (1) Prepare a heavy suspension of the culture in a few drops of distilled water.
- (2) Make a smear in the usual manner.
- (3) Fix in a flame.
- (4) Flood for 30 to 60 seconds with 5% aqueous Malachite green heated to steaming 3 or 4 times.
- (5) Wash off excess stain in tap water.
- (6) Counterstain 30 seconds with safranin. The spores should be green and the rest of the cells red.

A much simpler method is based upon the use of crystal violet. In this method, the microorganism is stained for 30 seconds so that the stain is insufficient to penetrate most of the spores. Thus, the spores appear as very light portions within the vegetative cell which is deeply stained.

A photomicrograph of a sporeforming bacteria (*Bacillus pumilus*) is shown in Figure XIV-2 taken at a magnification of 525. The spores are visible as the lighter portions in the center of the organism.

Use of Capsule Stain. An important consideration in microbiology is whether bacteria are encapsulated or not. Capsulated bacteria are particularly troublesome in paper mill systems, since they are great slime producers. There are several capsule stains which can be used. All these are rather difficult to apply, but Gin's method appears to be the best.

Gin's method involves the use of India ink and carbol fuchsin. The procedure is as follows:

- (1) Prepare on a slide a droplet of suspension containing the bacteria.
- (2) Place near this droplet an equal volume of India ink.
- (3) Mix the two with a loop; then spread by means of a second slide drawn evenly over the first.
- (4) Dry in the air and fix with a flame.
- (5) Stain 30 seconds with carbol fuchsin.
- (6) Wash in tap water and blot dry.

The capsules will appear as colorless halos surrounding reddish stained cells.

Capsules may be from 0.5 to 2.0 microns and sometimes up to 6.0 microns in thickness. A capsulated bacterium (*Aerobacter aerogenes*) is shown in Figure XIV-3 at a magnification of 525. The capsules are visible as the lighter area around the cell proper.

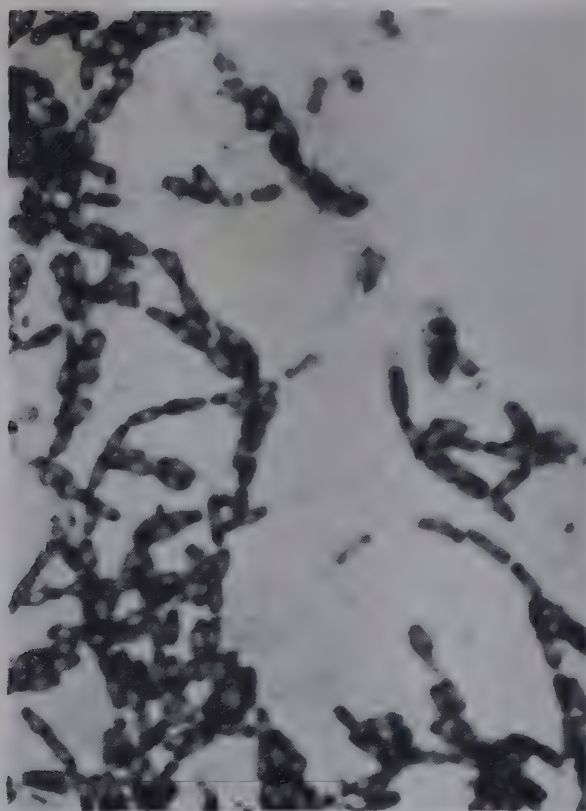


Fig. XIV-2. *Bacillus fumilus* showing spores (525 \times). Courtesy National Aluminate Corporation.



Fig. XIV-3. *Aerobacter aerogenes* showing capsules (525 \times). Courtesy National Aluminate Corporation.

Fungi

Fungi are multicelled plants which grow in the form of long threads or filaments. Conditions in the paper mill are quite favorable for the growth of fungi, and often they will grow quite luxuriantly, producing slimes which often break away in large pieces. Most fungi are aerobic and grow best where oxygen is plentiful. They are, as a class, more resistant to heat and chemicals than the bacteria or algae, and hence are usually more difficult to destroy. Fungi prefer an acid medium.

Fungi can often be identified by the appearance of the growth, although the only positive means of identification is by the type of spore formation. There are nearly 100 different fungi which turn up from time to time in paper mill systems, but there are only about ten to twenty species which may be considered as highly active. There are two principal types of fungi which are of interest to the paper chemist, the mold type and the yeast type.

Mold Type Fungi. The mold type (filamentous) fungi consist of fine strands which bear a head containing the spores. The spores usually grow in a typical cluster on the end of the conidiophore or stalk. Important members of the filamentous or mold type fungi are *Penicillium*, *Fusarium*, *Trichoderma*, *Alternaria*, *Spicaria*, *Botrytis*, *Citromyces* and *Aspergillus*.

The growth of *Aspergillus* is generally granular, and once seen, this organism can usually be recognized by this characteristic. The color of the growth is helpful: e.g., *A. niger* group is black, *A. fumigatus* group is blue-green, *A. candidus* group is white, *A. wentii* group is coffee-colored, *A. glaucus* group is green. A photograph of *Aspergillus niger* taken at 575 \times is shown in Figure XIV-4.

The *Trichoderma* species can be identified by the fact that the spores grow in tight bunches on the end of a pointed conidiophore, as shown in Figure XIV-5, which is a photomicrograph of *Trichoderma kőningi* taken at 55 \times . The growth is typically open and is usually green in color.

The *Penicillium* species are typified by a branched conidiophore. The colors are usually yellow-green and brown.

Yeast Type Fungi. The spores in yeast type fungi do not grow in a head at one end of the conidiophore, but instead are formed at the side of the filament by a process known as budding. Among the most important yeast type fungi found in paper mills are *Oidium* and *Monilia*. A photomicrograph of a species of *Monilia* taken at 250 \times is shown in Figure XIV-6.

Effects Produced in Pulp Systems

Excessive growth of microorganisms in paper mill systems leads to many undesirable effects which interfere with the normal operation of the mill and sometimes make the final product unfit for use. The two principal results of excessive microbiological activity are slime production and cor-



Fig. XIV-4. *Aspergillus niger* (575 \times). Courtesy National Aluminate Corporation.

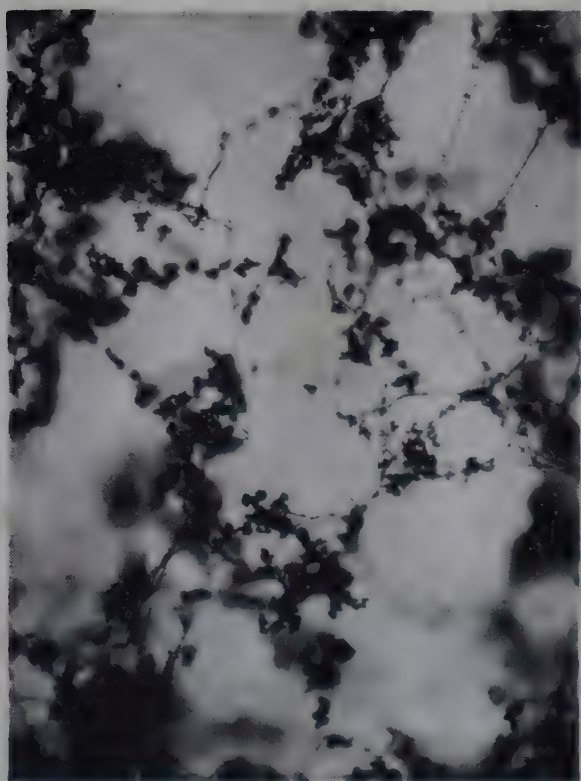


Fig. XIV-5. *Trichoderma köningi* (55 \times). Courtesy National Aluminate Corporation.

rosion, but there are many other troubles caused by microbiological growth, including decomposition of the cellulose, creation of bad odors, and spotting of the paper. The following section discusses some of the more important effects which should be considered by the paper chemist.

Slime Formation

Every paper chemist is familiar with mill slime, although it is not as prevalent today as it was before the introduction and widespread use of toxicants. The papermaker is constantly troubled with slimy or gelatinous accumulations which adhere to the inside of pipelines, chests, and screens, and in particular form on the exposed spiders of cylinder machines and along the edge of the wire pit on Fourdrinier machines. A slippery feel on

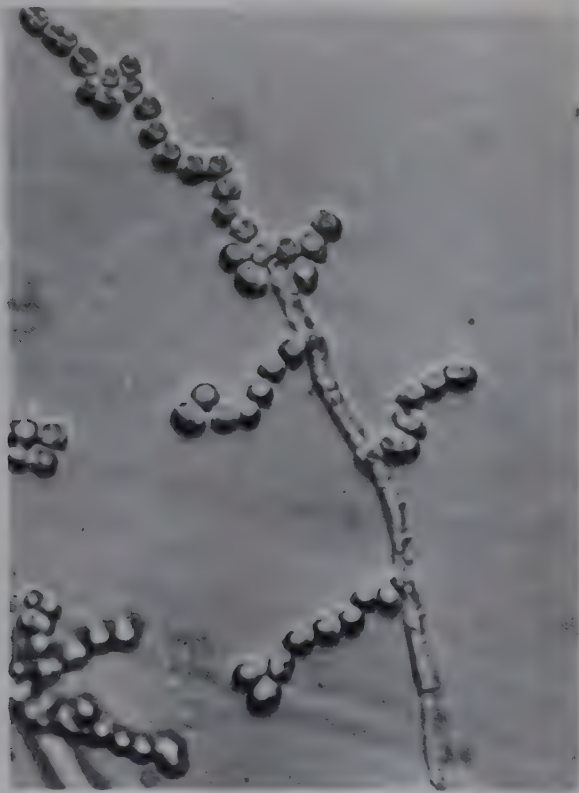


Fig. XIV-6. *Monilia* (white) (250 \times). Courtesy National Aluminate Corporation.

any of these surfaces is an indication of slime. The deposits frequently grow to such size that they break loose from their point of attachment and are carried along with the stock to the paper machine where they cause trouble with clogging of the felts and wires and breaks on the paper machine. Today, most mills try to keep slime under control through frequent wash-ups and the use of toxicants. Slime can build up in the paper mill system unnoticed, and the first indication may be breaks on the machine and the production of dirty paper. Careful examination of the machine and use of slime-measuring boards (discussed later) are the best indication of slime build-up.

Slime formation is undesirable for the following reasons: (1) it means

economic losses; (2) it reduces the effective diameter of pipelines; (3) it frequently plugs wires and felts; (4) it interferes with sheet formation; (5) it reduces the strength of the sheet; (6) it detracts from the appearance of the sheet; (7) it creates odors in the system; and (8) it protects and encourages the growth of anaerobic corrosion-producing bacteria.

Slime varies from soft, gelatinous, rubbery, or stringy matter to hard or horny growths. Usually it is submerged in the pulp system, but spatter slime, which forms at or above the water line, is also quite common. Ordinarily, mill slime consists of a mixture of microorganisms, fibers, and debris, all matted together. Slime usually contains some form of hemi-cellulosic material, probably a levulan, galactan, arabin, or cellulan, which swells in water but does not dissolve in water, or even in solutions of dilute alkali or acid. Each of the various groups of microorganisms produces a characteristic form of slime.

Bacterial Slime. Bacteria are one of the principal causes of slime in the paper mill system, and both the sporeforming and the non-sporeforming bacteria are guilty. The slime-producing bacteria convert excess food substance in the pulp system into slimy material. This material may diffuse away from the organism to produce slime in other locations, or it may act as a coating or sheath about the body of the organism. The latter is called a capsule, and it may be distinguished from the organism proper by staining (see Fig. XIV-3). In either case, slime acts to protect the bacteria from the adverse effects of heat, dryness, and chemicals, so that organisms embedded in slime are difficult to destroy.

Usually the rod-shaped bacteria are responsible for slime, although the round or cocci forms may also contribute.⁸ Some of the genera frequently found in slime are *Aerobacter*, *Bacillus*, *Pseudomonas*, *Flavobacterium*, *Alealigenes*, *Cellulomonas*, *Achromobacter*, and the filamentous bacteria. The non-sporeforming bacteria (particularly *Aerobacter* spp.) are one of the most prolific slime producers, but fortunately they are easily controlled by toxicants. The sporeforming bacteria do not multiply as fast, but they form very tough, rubbery slime which is extremely resistant to heat and chemicals.^{9,10} The latter are likely to cause trouble in board mills. *Aerobacter* tends to produce gelatinous films, strands, or viscous masses of growth.¹⁰ The filamentous bacteria tend to enmesh other matter to form slimy accumulations, and the filamentous iron bacteria secrete ferric or manganese oxide within their capsule, thus giving rise to colored slime which often breaks away to cause staining in the paper.

⁸ H. K. Nason, R. S. Shumard and J. D. Fleming, *Paper Trade J.* 110, No. 13: 180-186 (Mar. 28, 1940)

⁹ J. A. Holmes, *Pulp Paper Mag. Canada* 46: 221-225, Convention Issue (1945)

¹⁰ J. A. Holmes, *Paper Trade J.* 113, No. 13: 164-166 (Sept. 25, 1941)

Fungal Slime. Slime is produced by fungi of both the mold type and the yeast type. Fungi may produce a gelatinous substance similar to that secreted by the slime-producing bacteria, but usually the slimy deposits formed by fungi are the result of tangled masses of filaments which entrap other ingredients, such as fiber, filler, and undispersed bits of coating. Such growth varies from small gel-like masses or hard, horny particles to matted, doughy, or granular accumulations which may be black or highly colored. Fungal slime is ordinarily loose and stringy in contrast to the firm, tough slimes produced by bacteria.

Growth from the filamentous (mold type) fungi tends to adhere to the inside of pipelines from which it breaks away in clumps. However, the slime occurs, for the most part, as spatter slime, that is, slime located at or above the water line in stock chests or on the machine parts.

The yeast type fungi produce accumulations of growth which are leathery or rubbery in consistency and extremely difficult to remove.

Corrosion

There is always some corrosion of metal parts in a paper mill, but it is one of the duties of the paper chemist to see that it never becomes excessive. Many conditions may be responsible for excessive corrosion, and one of these is the presence of certain types of bacteria.

In this connection, *Microspora desulfuricans*, which is a sporeforming vibrio, might be mentioned, since it has the ability to reduce sulfate compounds to sulfides and create a condition leading to further corrosion. The sulfide which is produced by this organism tends to react with soluble iron in the system to produce a black-colored insoluble iron sulfide. This results in a gradual wearing away of iron pipe and leaves a weak spot where the slime has accumulated. The process is essentially anaerobic, and the organism is found only under conditions of low air tension. It sometimes grows luxuriantly under slime produced by *Aerobacter aerogenes*, which protects it from the air. If the *Aerobacter* is eliminated, the *Microspora* will also be destroyed, since it then becomes exposed to the air. The hydrogen sulfide produced during the metabolism of these sulfate-reducing bacteria has been reported as neutralizing and precipitating the mercury ion of organomercurial, thereby reducing the effectiveness of this toxicant.¹¹

Other Effects

Aside from the principal problems of slime formation and corrosion, there are many other troubles which may be traced to excessive microbiological growth. The growth of fungi on wet-lap pulp or on paper which has been stored in damp places is often of serious concern because of discoloration.

¹¹ S. O. Pehrson, *Svensk Papperstidn.* 52, No. 9: 217-220 (May 15, 1949)

Other microorganisms are responsible for the creation of bad odors which are sometimes carried over into the paper. If such paper is used for the packaging of fatty foods such as doughnuts and potato chips the off-flavor may be transferred to the food. The offending organisms in this respect are those bacteria which have the ability to decompose sulfur-bearing compounds, thereby liberating offensive sulfur compounds such as hydrogen sulfide.

Some of the fungi have the ability to attack cellulose and break the chain molecules into shorter lengths. In extreme cases, this action results in a tenderizing or complete rotting of the fibers, with a resultant loss in tensile strength. However, the action is quite slow and serious loss in strength can occur only over a relatively long period of time. It is interesting to note that the resistance of cellulose to this attack depends to a marked extent upon the degree of polymerization of the cellulose, and that regenerated cellulose or partially degraded cellulose is much more susceptible than alpha cellulose. Clark¹² reports that bacteria increase the freeness of beaten stock left in a chest for a period of twenty-four to forty-eight hours, but in general, high bacterial counts in the fibrous system, or in the recirculated white water, even in the absence of excessive slime, result in a reduction in freeness.^{13, 14}

There are a number of wool-destroying organisms which attack paper mill felts, causing degradation and loss of tensile strength and thereby shortening the life of the felt.¹⁵⁻¹⁷ These microorganisms include a wide variety of bacteria and molds, all of which are characterized by the ability to liquefy gelatin.¹⁸ The *Bacillus* spp. seem to be most active, although *Pseudomonas*, *Proteus*, and *Alcaligenes* spp. are also active.

Other organisms secrete enzymes which have the property of decomposing peroxide. These may cause trouble in groundwood bleaching where peroxide is used as the bleaching agent.

Growth of Microorganisms

Microbiological growth can be controlled with assurance if the paper chemist has a general understanding of the growth habits of the causal organism. Growth is influenced by a large number of factors, and some of these are discussed in a general way in the following paragraphs. Among the most important are chemical environment, light, air tension, moisture.

¹² J. d'A. Clark, *Paper Trade J.* 97, No. 26: 311-317 (Dec. 28, 1933)

¹³ W. Rudolfs and N. L. Nemerow, *Tappi* 33, No. 7: 321-327 (July, 1950)

¹⁴ Annual Report, National Council for Stream Improvement, *Paper Trade J.* 130, No. 11: 22-28, 40 (Mar. 16, 1950)

¹⁵ J. W. Appling, *Paper Trade J.* 113, No. 13: 173-174 (Sept. 25, 1941)

¹⁶ J. P. Weidner, *Paper Trade J.* 110, No. 19: 262-264 (May 9, 1940)

¹⁷ L. McGrath, *Paper Ind.* 18, No. 4: 281-284 (July, 1936)

¹⁸ O. A. Smith, *Paper Trade J.* 113, No. 16: 203-205 (Oct. 16, 1941)

and temperature. In addition, Smyth and Obold¹⁹ point out that bacteria may be prevented from growing and may even be killed by shaking or by vigorous agitation. This is reminiscent of certain proteins which are coagulated by shaking.

Time of Growth

One of the most significant factors is the time element, since microorganisms require time in which to multiply. This is important, inasmuch as microorganisms do not cause trouble in small numbers. It is only after they have had a chance to multiply into the tens of thousands that microorganisms begin to create a troublesome situation.

In the paper mill system, microorganisms have a period of two to ten hours from the time they are introduced into the beater until they appear in the finished paper. In size solutions, adhesives, etc., which often stand around for several days, they have a much longer period in which to grow. In either case, the time is sufficient to produce a tremendous increase in the number of microorganisms, if other environmental factors are favorable.

Chemical Environment

Chemical environment is one of the most important factors controlling the growth of microorganisms. Certain elements are essential to growth and others are detrimental. Mineral salts, sugars, starches, other colloidal substances, and even cellulose may be utilized in the growth processes, and it is now believed that certain amino acids and even some of the vitamins may be essential. The growth of the filamentous iron bacteria is accelerated in the presence of iron salts. Definite requirements cannot be set up, however, since microorganisms have the ability to adapt themselves to new environmental conditions, and sometimes even to conditions which are normally quite toxic.

Certain operations in the paper and pulp mill are highly detrimental to growth. For example, cooking and bleaching generally destroy all life because of the toxic chemicals used in these operations. In some cases, the chemist deliberately creates unfavorable conditions through the use of toxicants.

Another highly important factor affecting growth is the *pH* of the medium. Bacteria require a neutral or slightly alkaline medium and generally grow best within a *pH* range of 6 to 8. Most bacteria do not grow below a *pH* of 5, and since the *pH* at the beater is often as low as 4.0 to 5.0, the growth of bacteria is inhibited at this point. This explains why the number of bacteria usually decreases after alum is added to the papermaking

¹⁹ H. F. Smyth and W. L. Obold, *Industrial Microbiology*, The Williams and Wilkins Co., Baltimore, Maryland (1930)

stock. In some cases bacteria produce acid by-products, and if these are allowed to accumulate, the organism poisons itself. However, this does not take place unless the growth has been exceptionally heavy. In contrast to the bacteria, the growth of fungi is not inhibited by low pH , since they grow well in acid media and usually thrive when the pH is between 3 to 7.

Light

Algae are the only microorganisms which require light for growth. As a result, algae are found only in places where there is abundant light, such as in outside water reservoirs. The fungi and bacteria do not require light and, in many cases, light actually inhibits their growth.

Air Tension

The available oxygen supply or air tension is another important factor, since microorganisms vary considerably in their oxygen requirements. As explained previously, a large group of bacteria called the aerobes require atmospheric oxygen, and another large group called the anaerobes, obtain their oxygen by indirect means and are poisoned by atmospheric oxygen. Still a third group, between these two and known as the microaerophiles or facultative group, utilize dissolved oxygen or oxygen from decomposed organic matter. In general, most paper mill organisms are aerobic. Some exceptions are the coliform bacteria and *Penicillium roqueforti*, which are facultative, and *Microspora desulfuricans*, which is anaerobic.

It should be pointed out that although air tension is important, it is often subordinate to other conditions. Many organisms live under conditions of unfavorable air tension.

Moisture

The amount of available moisture is one of the most important factors governing the type of growth. All microorganisms require some moisture, but certain microorganisms require more than others for optimum growth. Bacteria grow well in an excess of water and, as a result, bacterial slime is often completely submerged in water. Fungi grow well in moist places, but do not grow where it is excessively wet, and consequently fungal slime usually grows just above the water line. Fungi are responsible for the rotting and staining of wet-lap pulp and the mildewing of paper, where the relatively low moisture content provides an almost ideal condition for fungal growth.

Temperature

All microorganisms require heat for growth, and most grow best in a temperature range of 20 to 40° C. Excessive heat is harmful and even results in complete killing. Low temperature also inhibits growth, but it

only suppresses activity and does not kill. However, at -60°C ., most organisms are killed because the water in the organisms is frozen.

It is possible to divide organisms into three groups, depending upon the temperature range in which they grow best. These are the psychrophilic (cold-loving), mesophilic, and thermophilic (heat-loving). The minimum, optimum, and maximum growth temperatures in degrees centigrade are listed below for the different groups.

Group	Minimum temperature	Optimum temperature	Maximum temperature
Psychrophilic	0	10-20	30
Mesophilic	5-25	25-40	40-45
Thermophilic	40-45	50-55	60-80

An increase in water temperature such as takes place in the summer months generally means an increase in microbiological activity, particularly in northern paper mills. Ordinarily, the thermophiles are not much of a factor in paper mill systems, but in hot pulp systems such as those used in some board mills, the growth of thermophiles may be quite large. Rudolfs and Nemerow²⁰ found in laboratory studies that a temperature of 50°C . in the white water recirculation system was sufficient to inhibit microbiological activity.

Sources of Contamination in Mill System

Microorganisms are living bodies and, as such, can be reproduced only from other living bodies of the same type. Since pulp is sterile after cooking and bleaching, all growth in the paper mill system must arise from contamination which occurs subsequent to these operations. There are four primary sources of contamination, the water, the fibrous furnish, the non-fibrous furnish, and the air, and these will be discussed in the following sections.

Water as Source of Contamination

Of all the sources of contamination, the fresh water supply deserves the greatest consideration. Fresh water often contains algae, certain of the fungi, and various types of bacteria, including the capsulated and non-capsulated types and the filamentous iron types. At certain periods of the year water is likely to contain large numbers of bacteria belonging to the coliform group.

If the water contains a large number of microorganisms, it should be treated with a toxicant. Surface waters, in particular, should be regularly treated. Water obtained from deep wells may not require regular treat-

²⁰ W. Rudolfs and N. L. Nemerow, *Tappi* 33, No. 7: 321-327 (July, 1950)

ment, but even so, it should be checked periodically to see that a count of less than 100 colonies per cubic centimeter is maintained (method of plating described later).

The treatment of water with chlorine is discussed later in this chapter. Flocculation, sedimentation, and filtration of water are discussed in a separate chapter, since ordinarily these treatments do not affect the microorganisms in the water. Filtration may help to reduce the number of organisms, particularly if the water happens to have a very high count, but it is not effective by itself and may even increase the number of organisms if the filters are allowed to become infected with slime.

Fibrous Furnish as Source of Contamination

Next to the water supply, the fibrous furnish is probably the most important source of contamination. Pulpwood itself is a major source, and it is likely to be heavily contaminated with *Aerobacter*, particularly when the wood is taken from the bottom of the wood pile. A cinder bed under the pile helps to alleviate this condition.

When the wood is used in the manufacture of chemical pulp, there is no problem, since cooking results in a sterile pulp. Bleaching also sterilizes the pulp, so that it may be considered sterile when it leaves the bleaching plant. If the wood is used in the manufacture of groundwood pulp, the heat developed in grinding destroys all living cells except the heat-resistant ones.

Pulp is almost always contaminated during storage and shipment. Consequently, mills which purchase their pulp from outside sources have a more difficult control job than mills which cook and bleach their own pulp. Lap pulp often contains high counts of bacteria and is heavily infected with mold spores. This is particularly true in groundwood lap pulp. A bacterial examination of pulp is desirable to determine the number of colonies per gram of pulp.²¹

Mildewed pulp should never be used, since it acts as a potent source of contamination for the rest of the furnish. If, for any reason, mildewed stock must be used, precautions should be taken to see that the organisms causing the mildew are killed at the beater before they have a chance to produce slime in the paper mill system. As a rule, waste paper contains a large number of microorganisms and must be used with care if microbiological growth is to be kept under control. Virgin pulps are preferred for the surface of paper containers which is used in direct contact with foodstuffs.

Non-Fibrous Materials as Source of Contamination

The addition of non-fibrous materials such as starch, glue, and vegetable gums, to the furnish is often a source of contamination. However,

²¹ See TAPPI Standards

if the starch is cooked, it cannot be considered as a source of contamination. Even such materials as clay and rosin may be a source of contamination, although ordinarily they cause very little trouble.

Influence of Mill Conditions on Growth

Mill conditions have a pronounced effect on the amount and type of microbiological growth. Some of the important mill conditions are fibrous furnish, non-fibrous furnish, surfaces of attachment, and methods of handling white water. The introduction of toxicants in recent years has resulted in a shifting in types of microorganisms found in mill systems, because the removal of certain microorganisms has permitted other types to grow more freely.

TABLE I

TYPES OF MICROORGANISMS FOUND IN MILL SYSTEMS
Survey made in early 1940's showing number of cases
organisms were found in each group

Type	Groundwood mills	Chemical pulp mills	Chipboard mills
Sporeforming bacteria			
muroid	38	20	33
non-muroid	10	53	44
Fungi of mold type	90	33	33
Coliform bacteria, muroid	52	Neg.	28
Yeast type fungi	76	0	11
Micrococci, heat-resistant but non-muroid	Neg.	47	20
Putrefactive bacteria	Neg.	Neg.	28
Coliform bacteria, pollution	14	Neg.	22

Effect of Furnish on Growth

The types of microorganisms found in paper mill systems depend upon the fiber furnish. One of the most important factors is the amount of available food substance. Groundwood pulp is very rich in food substance; strawboard and waste papers are also rich in food substance; and chemical pulps are relatively low in food substance. However, nearly all pulp systems contain enough food to support a variety of microorganisms.

It is possible to divide paper mills into three groups on the basis of their microbiological activity: (1) groundwood mills, (2) chemical pulp mills, and (3) chipboard mills. Table I shows the typical flora found in the three different mill systems in the early 1940's, when chlorine was used in light doses as the principal toxicant.²² However, the flora has changed considerably in recent years as a result of the widespread use of improved toxicants, and the situation is still undergoing significant change.

²² Surveys made by J. R. Sanborn

Groundwood systems had a typical fermentation flora which included some or all of the following: (1) coliform bacteria, (2) yeast type fungi, and (3) mold type fungi. Thus, in the early days, groundwood furnishes abounded in mold type fungi and also contained a high percentage of yeast type fungi. Bacteria were also quite common, with *Aerobacter* predominating, and these appear to be attached to the fiber, since they are mostly removed on filtering of the pulp.²³ Groundwood is a particularly rich medium, and generally speaking, the higher the percentage of groundwood in a given furnish, the higher the total count. The following figures, which were taken from a board mill using a mixed furnish of groundwood and sulfite, illustrate this point.²⁴

Groundwood in furnish, %	Total count, colonies/cc.
90	900,000
75	700,000
55	300,000
35	35,000
0	4,000

Mills using chemical pulp had a heat and chemical-resistant flora which was composed principally of the following: (1) sporeforming bacteria, (2) micrococci, and (3) filamentous bacteria. As a rule, the total count is low but the organisms are difficult to destroy.

Chipboard mills tend toward a miscellaneous flora which include those organisms found in both chemical and groundwood mill systems, as well as the putrefactive organisms commonly found in waste paper. In fact, any type of organism may be found in a chipboard mill, and the count is usually high. The species include mucoid varieties of the mold type fungi, sporeforming bacteria, and non-sporeforming bacteria of the coliform group. Thermophilic organisms are also found, since the temperature of the stock is often as high as 55 to 60° C.

Microbiological activity is affected by certain of the non-fibrous materials commonly added to the beater furnish. Proteins (e.g., glue or casein) appreciably stimulate microbiological activity; starch has a slight stimulating effect; rosin has no effect.²⁵ Alum has an inhibiting effect. Clay, of course, is not subject to microbiological decomposition, but clay sometimes increases slime difficulties by forming a nucleus around which slime develops in a form known as "tapioca" slime, a condition of round, white, jelly-like particles.²⁶

²³ J. S. Reichert, R. T. Mills and D. J. Campbell, *Paper Trade J.* 122, No. 5: 41-43 (Jan. 31, 1946)

²⁴ Survey made by J. R. Sanborn

²⁵ W. Rudolfs and N. L. Nemerow, paper presented at 35th Annual Meeting of TAPPI, New York City (Feb. 20-23, 1950)

²⁶ R. E. Hayes, *Pulp Paper Mag. Canada* 37: 102-104, Convention Issue (1936)

Effect of Surfaces of Attachment on Growth

One of the important mill factors influencing growth is the type of surface which is available for attachment of the microorganism. All slime-producing organisms tend to attach themselves to rough or porous surfaces, and for this reason, rough surfaces should be avoided whenever possible. This is particularly important in chests, tanks, or pipelines which are difficult to clean.

From a microbiological standpoint, glazed tile is excellent for chests because of its extremely smooth, non-porous surface. Wood tanks are undesirable because of their porous nature which makes them difficult to keep clean. Microorganisms held within the pores of wood tanks are often responsible for the spoilage of glue or starch solutions. The same situation exists in wood calender boxes, and for this reason, wood boxes should be lined with linoleum or some similar material.

When it comes to piping, there are many materials which might be used. Glass piping is almost ideal, since it has a smooth, non-porous surface, and permits observation of its content. Asbestos-cement pipe is excellent because it does not corrode, but it is lacking in resistance to acid solutions. Iron pipes are the most widely used, but they are not completely satisfactory. Copper piping is better, but is rather expensive. In any event, the piping should be well located and arranged for easy cleaning, since in cases of extreme contamination, it may be desirable to disassemble it for cleaning.

Methods of Handling Process Water and Stock

Another very important factor in controlling microbiological growth is the method of handling process water and stock. As has already been pointed out, there are several stages where the pulp is sterilized as, for example, at the end of the cooking and bleaching processes, and there are other stages where the amount of growth is greatly reduced as, for example, at the pulpstones in the groundwood mill and at the end of the paper machine drier section. On the other hand, there are points in the process where conditions are highly favorable for growth. The greatest growth usually takes place during the advanced stages of paper manufacture, i.e., at the deckers, chests, and headboxes of the paper machine, and any circulation of water from these points to an earlier stage of the process results in contamination of the pulp at that point. For example, any circulation of white water to the blowpit of the pulp mill or to the grinder of a groundwood mill will result in contamination at these points. White water, particularly white water which has been held in storage for a long time, often contains resistant strains of microorganisms which have become acclimated to the mill system and, as such, are particularly difficult to control. Furthermore,

even though the water contains no vegetative (growing) cells, it may contain spores which are capable of germinating later. For this reason, it is best to use fresh, treated water at the showers for cleaning felts, for making up sizing solutions, etc. Best results are obtained by keeping the systems in the mill independent of one another.

Paper mill broke is another material which is recirculated in the mill and consequently is capable of spreading contamination from one spot to another. Wet broke is much worse than dry broke, since the latter is usually partially sterilized by the heat on the driers. The air is another medium which may act as a carrier, since it is capable of spreading spores from fungi.

Seasonal Variations

It should be pointed out that the microflora in the mill system is constantly changing, since it is influenced by seasonal changes, changes in pulp supplies, condition of fresh water, changes in chemical environment, etc. Slime may occur the year round, but slime troubles are more prevalent during certain months of the year. The character of the slime varies seasonally and, as a general rule, summer slime tends to be hard and compact, whereas winter slime tends to be loose and stringy.

Seasonal variations depend to a large extent upon the latitude in which the mill is located, but the biggest factor is the type of control program, since mills with adequate control are ordinarily not greatly affected by seasonal variations.

Generally speaking, there are two difficult periods of the year for northern paper mills. The first of these is in the spring months, from February to June, when the organisms likely to show up include the rapid growing, non-sporeforming bacteria (*Flavobacterium* and *Aerobacter*) and the fungi (*Aspergillus*, *Monilia*, *Oidium*, and *Torula*.^{26a} Certain of the spore-forming bacteria (*Bacillus subtilis* and *Bacillus megatherium*) may also show up at this time, although they are more likely to turn up a little later in July. The yeast type fungi (*Monilia* and *Oidium*) are also likely to extend into July. The second difficult period usually is in the fall months of October and November, particularly in those mills using surface water, since surface water is likely to be contaminated at this time of year with microorganisms picked up from decayed leaves, grasses, and other vegetation. Some of the microorganisms most likely to appear during this period are *Aerobacter*, *Monilia*, *Flavobacterium*, *Penicillium*, *Oidium*, and *Trichoderma*. During December and January there is usually a second lull in activity comparable to that occurring in August and September.

Several factors are responsible for the seasonal variations noted above. Temperature plays some part, particularly in northern mills where the

^{26a} Material on seasonal variations largely taken from notes obtained from lectures by J. R. Sanborn in course given at Syracuse Univ.

water is likely to increase as much as 25° C. over the average winter temperature. However, temperature is not the entire explanation, since it does not explain the lull in microbiological activity occurring during the months of August and September. This lull is caused by the toxicant residual which has been built up in the mill system as a result of the increased dosage of toxicant which is added at the time of the spring flare-up. In other words, the full effects of this increased treatment are not obtained until a month or two later, which indicates that the control measures were poorly timed. It is now considered better practice to make preparation ahead of time by gradually building up the dosage of chlorine and other toxicants in March and April to avoid the flare-up which ordinarily occurs in May and June. Likewise, corrective measures should also be applied early in the fall months to prevent the flare-up which normally occurs in September and October. If this schedule is followed, that is, if toxicants are applied in larger dosage early enough in the spring and fall, there will generally be no seasonal flare-up.

Control in Pulp System

The objective of the chemist or bacteriologist, so far as microbiological activity in the paper mill system is concerned, is to keep the growth under control so that none of the difficulties previously mentioned can develop. This is accomplished mainly by observing a high degree of cleanliness and, if necessary, using toxicants to inhibit or prevent further growth. The problem has been quite serious, as shown in a mill survey made by Appling and coworkers²⁷ in 1943, in which one-quarter of the mills reported that slime control was highly unsatisfactory. Today, however, the situation is much more satisfactory, on account of the increased attention given to the subject of microbiology.

Mill Survey

A satisfactory mill survey should list (1) the sources of contamination, (2) the points where growth is excessive, (3) recommendations for control, and (4) indications of the effectiveness of the various treatments. A complete survey requires several weeks and should include not only a count of the number of microorganisms present but also a listing of the general types present and comments upon their characteristics. In making a mill survey, the following points are suggested for sampling: raw water, treated water, pulp, starches and other materials added at beater, sample from the beater, sample from broke beater, stock in chests, stock in headboxes, stock in vats of cylinder machines, white water, broke, calender boxes, and wet paper.

²⁷ J. W. Appling, J. F. McCoy and B. F. Shema, *Paper Trade J.* 124, No. 22: 239-250 (May 29, 1947)

A mill survey is desirable before an intelligent program of control can be instituted. The mill survey should be made at least twice a year, and more often in some cases. The knowledge gained from a mill survey is very useful, since it is much better to suppress growth at its source before it has a chance to develop than to try to control it later. For example, it is far easier to destroy microorganisms in the fresh water supply than in the paper mill system after these microorganisms have had a chance to develop protective coatings of slime. For the same reason, the pulp supply and non-fibrous raw materials should be checked and corrective measures applied before slime develops. Waste papers are always badly contaminated, and hence it is usually desirable to add toxicant at the breaker beater. If a certain spot in the mill system shows a high count, then toxicant should be added at that point, or the flow of stock should be streamlined in such a way as to prevent stagnation.

Slime-measuring units²⁸ are available for use on the wet end. These determine the weight of slime accumulating in a given period of time on a certain area of wooden, rubber, or cement panel mounted in a stainless steel housing connected at an appropriate spot in the paper mill system. Plating is frequently used to determine the count of organisms in the components of the furnish at various points in the stock system or in the finished paper.

The relative value of mill surveys based on bacterial counts versus the value of slime-measuring units is a highly controversial issue. Some mills achieve outstanding results in slime control by use of slime-measuring units without making a mill survey of the type described above, whereas other mills feel that slime-measuring boards too often indicate nothing directly related to slime control. However, slime-measuring units are used in many mills and their method of use is described later.

Plating. Plating consists of inoculation of sterile agar medium with a small amount of the test sample and pouring of the mixture into a Petri dish where it is allowed to cool. Plating methods are useful for two reasons: (1) because they indicate the number of microorganisms present in the sample, and (2) because the microorganisms can sometimes be identified from the appearance of the growth.

Agar is used in the plating medium to cause solidification on cooling. A nutrient or foodstuff must also be present in the medium. A number of different media are used, and these can be purchased from supply houses and prepared by mixing with water and sterilizing in an autoclave.

The first step in plating is dilution of the sample. Dilution is necessary because most samples in their original state contain so many microorganisms that they produce overcrowded plates. Dilution is carried out by using sterile dilution bottles containing 99 cc. of sterile water. To the

²⁸ Buckman Laboratories, Inc., Memphis, Tennessee

first bottle is added 1 cc. or 1 g. of the material to be tested. This bottle is then thoroughly shaken and 1 cc. of its contents is added to the second bottle. This bottle is shaken and 1 cc. of the contents is added to a third bottle, and so on. In this way the original sample is diluted in the ratio of 1 to 100, 1 to 10,000, 1 to 1,000,000, 1 to 100,000,000, etc.

The second step in preparing a plate consists of pipetting 1 cc. from each of the dilution bottles and adding to separate sterile Petri dishes. (A Petri dish consists of two circular glass dishes, one of which holds the sample, and the other acts as a cover to protect the sample from contamination.) Enough agar medium is then added to each Petri dish to cover the bottom of the dish, after which the dish is rotated gently to distribute the sample throughout the agar. It is important that the agar be added while not too hot, since this destroys the microorganisms. On the other hand, the agar must not be too cool, since it will be too viscous to mix properly. After the agar and sample are thoroughly mixed, the plate is cooled for about twenty to thirty minutes, or until the agar has solidified. Finally, the dish is incubated in an inverted position (which prevents condensation from dropping on the agar) for forty-eight hours at a temperature of 28 to 37° C. Temperatures of 28 to 30° C. are preferable for the incubation of molds, whereas a temperature of 37° C. is preferable for the incubation of bacteria.

One of the most useful plating methods is the so-called total count obtained on tryptone glucose agar.

Tryptone glucose agar contains: beef extract, 3 g.; tryptone (casein digest), 5 g.; glucose, 1 g.; agar, 15 g.; water (distilled), 1000 cc. It can be obtained from DIFCO Laboratories, Detroit, Michigan.

Plates prepared with tryptone glucose agar, as described above, show the total number of "colonies" which grow from individual bacteria or clumps of bacteria. In other words, the total count gives the number of *colonies* of bacteria which develop after plating appropriate dilutions of the sample under the specific conditions just outlined, and is reported as number of colonies per cubic centimeter or per gram of original sample.

The total count is useful because it indicates points in the mill system where growth is taking place and also measures the extent of this growth. A high count indicates that conditions are favorable for growth and, if slime is not already present, that it will likely develop in the future. High counts are a potential source of trouble and steps should be taken to reduce the count to a reasonable level, even though no trouble is being experienced at the time. A zero count is not required in most cases and may even be undesirable in that it signifies a wasteful use of expensive toxicant. The acceptable count depends entirely upon the grade of paper being manufactured, and at present the subject is highly controversial, no universal stand-

ard being acceptable to the industry. It is possible only to make broad generalizations, such as mills which keep their total count below 250 to 500 colonies or less per gram of fiber can be said to be doing a reasonably good job of control, whereas mills which consistently maintain counts in the hundreds of thousands can be said to be doing a poor job.

In combination with the total count made on tryptone glucose agar, it is useful to make a count in the same manner, using potato glucose agar, an exceedingly rich medium on which the slime-producing organisms outdo all others. The high carbohydrate content of potato glucose agar medium causes it to produce typical slimy or mucoid growths, and in this respect, it is equivalent to a rich groundwood pulp. A count on potato glucose agar indicates the microorganisms which are likely to be troublesome from the standpoint of slime production.

Potato glucose agar can be obtained from supply houses, but the following is recommended as a more suitable medium for paper mill work: potatoes, 400 g.; agar, 25 g.; glucose, 25 g.; distilled water, 1000 cc.

Peel and cut the potatoes into thin slices and then boil in water in a pan placed in an autoclave for 30 minutes at 15 lb. pressure. Strain the potatoes through three layers of cheesecloth, taking care to get only the liquid portion from the potatoes and no sediment. Add water up to 1000 cc., and then add agar and glucose and heat until the agar is melted. Then pour into Erlenmeyer flasks, stopper with cotton, and autoclave at 15 lb. pressure for 20 minutes to sterilize.

Sometimes an acidic potato glucose agar is made by adding 6 cc. of a 10% tartaric acid solution to 300 cc. of liquefied potato glucose agar. This acid medium inhibits the growth of bacteria, but promotes the growth of fungi.

Potato glucose broth is made in the above way, except that no agar is added.

Cleanliness

Effective control of microorganisms is based on remedial as well as preventive measures. Cleanliness is perhaps the most important single factor in the control of microbiological growth. Cleaning is the first step in any control program, because the application of toxicants to a "dirty" system is a wasteful use of expensive material. The use of toxicants is a secondary consideration, since they will be only partially effective if the system is not clean.

Cleanliness means the observance of ordinary good housekeeping practice, such as not throwing trash and floor sweepings into the broke. It also includes the observance of rules of sanitation, which means that the microbiologist must be on the lookout for small localized sources of growth. Even small spots of growth which are not readily visible are sufficient to contaminate the entire paper mill system, if they are left untouched. Slime, excessive corrosion, bad odors, etc., are symptoms which occur after the damage has been done. It is a part of the microbiologist's function to ward off trouble before it becomes serious, and this can be done by making

periodic mill surveys. A properly conducted survey will locate the focal points of infection and serve as a check on the control measures which are being used.

The correct layout of the mill system is important in the maintenance of proper cleanliness. The wet end system should be streamlined to prevent accumulations of stock or slime in dead-ends or pockets, since slime is less likely to form in stock which is in fairly rapid motion. Slime pockets in seal boxes, flumes, tanks, etc., are sources of infection where organisms may thrive and spread to colonize other parts of the mill. Another important factor which has already been mentioned is the use of equipment which has a smooth, non-porous surface. Old corroded or roughened pipe should be replaced. Any tendency for the stock to spatter on the walls should be held to a minimum.

The basis of cleanliness is frequent wash-ups of the mill wet end system: The first step is the removal of all slime and accumulations from tanks, pipelines, and machine parts. Wash-ups usually take place over the weekend, but it is sometimes advisable to prepare for them ahead of time by stepping up the dosage of toxicant toward the end of the week. Wash-ups should be carefully planned to avoid excessive downtime. Some slimes are hard and horny and are difficult to remove, once they have been allowed to dry out. With these, alkaline slime removers may be desirable for softening the slime and making it easier to wash off. Other slimes are so hard that they can be removed only by scraping or by scrubbing with brushes. One method used in cleaning the wet end comprises the following technique.²⁹ A solution of alkaline slime remover is made up in the beater at a concentration of about 2 to 4 oz. per gallon of water. The solution is manually brushed on the slime-covered spots in the beater and then dropped into the stock chest where it is manually brushed on slime there. Then, the solution is pumped through the piping system, jordan, and into the jordan chest. Recirculation for a period up to two hours may be necessary for complete removal of slime. The solution should be maintained at a high temperature (120 to 180° F.) during this period by reheating. All exposed portions of equipment should then be scraped, if necessary, and the whole system hosed out with hot water. All slime deposits removed during the cleaning operation should be run to the sewer. Blancol (sodium salt of a condensed naphthalene sulfonic acid) plus caustic soda and Oakite (#22) are some of the alkaline cleaning agents used for slime removal in the above way.

Once the system has been washed and scraped clean, it should be sterilized to make certain that all organisms are destroyed. Heat is an effective sterilizing agent and, in this respect, very hot water is better than steam. Combinations of heat, toxicant, and penetrant may be used by washing with

²⁹ R. Kipp, *Paper Mill News* 73, No. 11: 10 (Mar. 18, 1950)

water at 180° F. containing both a detergent and a toxicant. A contact time of at least two hours is recommended. Soderberg³⁰ recommends the use of a dispersing agent, a bactericide, and a fungicide.

One of the best disinfectants is bleach liquor. The solution should have an odor of bleach, or should contain in the neighborhood of 0.25% available chlorine. In cleaning tanks made of wood, the liquor should be allowed to remain for an appreciable length of time, preferably overnight, so that the organisms in the pores of the wood are completely destroyed. Another widely used germicidal solution is water containing a high chlorine residual of 1 to 2 p.p.m.

The calender stacks should be given particular attention when water boxes are used, since it is not uncommon to find cases where the paper is fairly sterile coming from the driers, but it is recontaminated by water or starch solution at the calender stack. Most sizing solutions applied at the calender stack or sizing tub are subject to spoilage and should be protected with a toxicant or kept under constant supervision, particularly when the paper or paperboard is to be used for packaging foodstuffs. The construction of calender boxes is very important, and paper wadding should never be used to plug the ends of the boxes unless it has been dipped in a solution of toxicant. When extreme care is warranted, the paper should not be touched, except with clean hands, and the rolls should be carefully wrapped as soon as possible and stored in a clean, dry place.

After the wet-end system has been thoroughly cleaned and operations resumed, the next step involves the suppression of growth through the use of toxicants.

Resistance of Organisms to Toxicants and High Temperatures

There is an appreciable difference among the various microorganisms in their resistance to toxicants and high temperatures. For this reason, preventive and remedial measures should be applied with as much knowledge as possible of the types of microorganisms involved.

Occasionally the killing or inhibition of one group of microorganisms results in the increased growth of another type which was inhibited by the presence of the first group. As microbiological activity is reduced, the microorganisms remaining behind become increasingly difficult to kill. Some microorganisms which were quite prevalent years ago are almost never found in a well-kept mill today. These were the microorganisms which were quite susceptible to toxicants, whereas those which are prevalent today have a greater resistance. Preservation of biological competition in the residual flora is helpful in reducing over-all activity. Appling³¹ and co-

³⁰ F. A. Soderberg, *Paper Trade J.* 126, No. 22: 127-129 (May 27, 1948)

³¹ J. W. Appling, S. J. Buckman and C. D. Cash, *Tappi* 33, No. 7: 346-349 (July, 1950)

workers showed that groundwood treated with a large amount of phenylmercuric acetate exhibited appreciable mold growth, while groundwood treated with a small amount was much freer of mold growth. It is believed that the large amount of chemical killed off certain bacteria which have a marked antibiotic effect on *Penicillium roqueforti*, an organism which has a high resistance to phenylmercuric acetate.

Several factors affect the resistance of microorganisms to toxicants and high temperature. One of the most significant is the presence or absence of slime, since organisms which are embedded in slime are more resistant than those which are exposed, because slime protects the living organism from the destructive effects of heat or chemicals. The capsulated bacteria are very hard to destroy. In attacking slime-producing organisms, it is best to destroy the organism before it has a chance to produce slime. For example, bacteria in the coliform group are fairly easy to kill in the fresh water supply by chlorination, but once they have established slimy growths in the mill system, they become very difficult to eradicate. It should be pointed out that non-slime-producing organisms are not always easy to destroy just because they produce no slime of their own, since they sometimes become embedded in slime produced by other organisms.

The sporeforming organisms are particularly resistant, inasmuch as spores can withstand toxicants or high temperatures which destroy all vegetative cells. Morrison and Rettger³² found that although all vegetative cells are killed by holding bacteria at a temperature of 80° C. for ten minutes, the spores are not killed under these conditions. Thus, because of their spores, fungi and the sporeforming bacteria are more difficult to kill than the non-sporeforming bacteria, although these microorganisms can be controlled by reducing the growth of the vegetative cells. One anaerobic sporeforming bacterium, *Clostridium botulinum*, which causes botulism in food, can withstand a temperature of 120° C. for four minutes. *Actinomyces* is particularly difficult to control because its spores are both heat-resistant and not readily wetted with water.

Of the fungi, *Aspergillus flavus-oryzae*, *Cladosporium*, *Penicillium*, and *Monilia* are the most difficult to control, whereas *Oidium*, *Spicaria*, and *Tricoderma* are relatively easy to control. Of the bacteria, *Bacillus subtilis*, *Actinomyces*, and *Aerobacter cloacae* are most difficult to control, whereas *Achromobacter*, *Aerobacter aerogenes*, and *Escherichia coli* are relatively easy to control. These statements are only tentative, however, since new toxicants change the picture. If any microorganism in the difficult group is suspected, treatment with toxicants should be continued over a period of time, since these microorganisms have a tendency to reappear after the initial treatment.

³² E. W. Morrison and L. F. Rettger, *J. Bact.* 20: 289-311 (1930)

Use of Heat

The effect of temperature on the growth of microorganisms has already been discussed. It has been pointed out that each organism has an optimum temperature at which it grows best, but that extreme heat kills all microorganisms. There are a number of examples of the use of heat for controlling microorganisms, for example, the sterilization of the bacteriologist's equipment and canning of foodstuffs, but other than the lethal effect of the drier rolls, paper mill operators have made little use of heat as a control measure. Within recent years, however, there has been a greater use of hot water and steam for cleaning operations around the mill system. In many cases, heat is the cheapest means of destroying microorganisms. Hot water is often better than steam for the reason that it can be left in contact with the system for a longer period of time, and because it can be used to reach regions not readily accessible to steam.

Paper is heated to a high temperature while passing through the drier section so that there is, in most cases, a reduction in the bacterial content of approximately 98 to 99%.³³ In general, the non-sporeforming bacteria are completely destroyed, whereas the sporeforming bacteria may survive,³³ sometimes leading to an actual increase in the number of viable bacteria.³⁴ Hence, some other means must be used to insure complete destruction of the sporeforming bacteria.

Use of Toxicants

After the mill system has been thoroughly cleaned by means of water, scrubbing, heat, or other similar methods, the use of toxicants should be considered to prevent future growth. Usually an inhibiting dose, rather than a killing dose, of toxicant is used. In other words, enough toxicant is added to prevent rapid growth, but not enough to kill actually all microorganisms. Killing dosages are not used, since they are usually too expensive and are not really necessary. The paper chemist should keep in mind at all times that the dosage is merely inhibiting, and that the suppressed microorganisms may start multiplying at any time if the concentration of toxicant is allowed to fall below a safe limit.

The toxicant must come into contact with the microorganisms if it is to bring about killing or even inhibition of growth. Slime tends to prevent penetration of the toxicant, and for this reason it is more economical to apply toxicants before excessive slime has developed. There is frequently a time lag during which the toxicant penetrates the slime or the cell itself. Some toxicants penetrate faster than others, and hence are more efficient.

³³ J. W. Appling, *Paper Trade J.* 120, No. 6: 50-56 (Feb. 8, 1945)

³⁴ J. W. Appling and B. F. Shema, *Paper Trade J.* 114, No. 13: 40-44 (Mar. 26, 1942)

In early days toxicants were added only to the fresh water, but now they are added to recirculated white water and papermaking stock. Sterilization of the fresh water alone is not sufficient, since it is impractical to maintain enough residual toxicant in the fresh water to control growth throughout the mill system. The increased usage of white water has been responsible for this.

It should be realized that the method of application is often more important than the particular treatment selected for use. The toxicant must always be applied in such a way that it establishes direct contact with the microorganisms. The focal points must be reached with adequate concentrations of toxicant, which means that the toxicant must be added either at the focal points themselves, or in places where it will be quickly carried to these points. For best results, toxicant may have to be added at more than one point in the mill system. Toxicants are commonly added at the fan pump, headbox showers, and screens.

It is generally best to add the toxicant fairly rapidly over a relatively short period of time in order to maintain a high concentration for a short time. Appling and coworkers³⁵ found that this slug method of addition was the most effective for reducing slime in groundwood systems (as measured on slime boards, not by bacterial counts). In the slug treatment, one-half pound of toxicant was used for each ton of groundwood, and this was added about once every six hours. Other mills add toxicant once daily over a two-hour period. It is generally advisable to follow a weekly schedule in which a heavy treatment of toxicant is applied during the first few days, tapering off during the remainder of the week after slime formation has been inhibited.³⁶

The system of control varies with each mill, and no general rules can be given. A satisfactory system may include the following: (1) chlorination of fresh water, (2) addition of chloramine at the chests or white water system, and (3) addition of chlorinated phenols or organic mercury compounds to the mill system.

There are many other uses for toxicants besides that of controlling growth in the mill system. Wood pulp, to be stored in lap form, is often treated. Paper or paperboard may be treated to prevent molding. Toxicants may be used for treating felts on the paper machine to increase their life. Toxicants are also widely used for preserving sizing solutions, adhesives, etc. For each of these purposes, it is necessary to select a toxicant which best suits the specific flora, mill conditions, or other requirements, since no one toxicant is a cure-all. Some of the various commercial toxi-

³⁵ B. F. Shema, J. B. Anderson and J. W. Appling, *Paper Trade J.* 127, No. 19: 447-453 (Nov. 4, 1948)

³⁶ E. L. Neal and S. F. Jennings, *Pulp Paper Mag. Canada* 49, No. 3: 137-142, Convention Issue (1948)

cants available at the present time will be taken up in the following sections and their various uses discussed.

Use of Chlorine. Chlorine has been widely used as a toxicant in the paper industry since about 1910. It is an effective bacteria-killing agent and, as such, makes an excellent toxicant for treating raw water to destroy potential slime-forming bacteria. Raw waters should be treated with chlorine before they enter the water-treatment plant. Water carrying a residual of 1.0 to 1.5 p.p.m. of chlorine is useful as a bacteria-killing solution for wash-ups. In some groundwood mills, chlorinated water is used throughout the wood-handling operations on log-hauls, barkers, etc. Chlorine has certain limitations, since it is not completely effective against the spore-forming bacteria or the fungi.

Chlorine may be used in many different forms. It can be added directly to water or papermaking stock by means of special chlorinating apparatus, or it can be used in combination with ammonia to produce chloramines. Chlorine can also be used in the form of hypochlorite for cleaning tanks, pipelines, etc.

The efficiency of chlorine as a bactericide depends upon concentration, reaction time, temperature, and pH. The pH should be relatively low, since hypochlorous acid is the most active agent. The killing time decreases appreciably at pH values over 7 and is greatly delayed at pH 10. High temperature is beneficial, and Miller³⁷ found that the time for killing was reduced approximately 50% for each 10° C. rise in temperature between 20 to 50° C.

Before the widespread reuse of white water, direct chlorination of the fresh water was the only precaution needed to control microbiological growth in the paper mill system. The presence of low residuals of chlorine in the fresh water was adequate, because fresh water was used throughout the mill in showers, for dilution, etc., and hence carried a slight sterilizing action throughout the mill. In later years, when mills adopted a program of white water reuse, white water was used in place of fresh water at the showers. Thus, instead of adding fresh make-up water with germicidal properties, white water, which was often badly contaminated, was used. Chlorine was still added to the fresh water, but not in sufficient quantity to carry through the mill system and suppress growth.

Chlorine is extremely reactive and tends to combine with organic matter to form addition and substitution compounds. This means that chlorine is quickly dissipated by reaction with lignin and other materials in the paper mill system, and thus is relatively ineffective in pulp systems. However, chlorine is admirably suited for raw water treatment where it checks

³⁷ L. B. Miller, *Paper Trade J.* 116, No. 16: 173-182 (Apr. 22, 1943)

the growth and destroys microorganisms before they have a chance to produce slime in the mill system.

Chlorine is effective in eliminating tastes and odors in water due to algae, dissolved organic matter, or trade wastes. This is a rather new development brought about by break-point chlorination. Up to the time of break-point chlorination, most mills used chlorine as sparingly as possible, with the result that there was no true chlorine residual (although there may have been a chloramine residual). Break-point chlorination involves adding sufficient chlorine for a long enough time to destroy completely the chloramines and any taste- and odor-producing substances in the water. This is done by applying chlorine until there is a residual of free available chlorine, either as hypochlorous acid, free chlorine, or hypochlorite, so that offending substances are destroyed and the system becomes relatively stable.³⁸ Break-point chlorination is based upon the following facts. When chlorine is added to water, the residual or unreacted chlorine first increases, but later recedes toward zero. As more chlorine is added, the residual chlorine again rises, but this time at a uniform rate, since the chlorine demand has been satisfied. The point at which this second rise takes place is called the break-point, and its significance is that it represents the point beyond which there is no further reaction between the chlorine and organic matter present in the water.³⁹ Stated differently, the chlorine demand increases as chlorine is added up to a definite point (the break-point), after which the chlorine demand remains constant. The chlorine demand is defined as the amount of chlorine consumed by the water under specific conditions of time, temperature, etc. At the break-point, there is free available chlorine, and hence the oxidation potential is great enough to destroy all nitrogenous matter. In break-point chlorination, the water is treated with the required amount of chlorine and is allowed to react for sufficient time prior to the use of the water.

It has been claimed³⁸ that chlorination to the point of a chlorine residual kills 95 to 99% of all microorganisms within a few minutes. This is true for most microorganisms, but there are a few difficult microorganisms such as *Aerobacter cloacae*, *Alcaligenes*, and *Pseudomonas*, which require fairly high residuals, often in the neighborhood of 1 to 2 p.p.m. Fungi are, as a rule, not greatly affected by chlorine, unless large amounts are used. Generally they cannot be controlled by chlorine in acceptable use concentrations.

News and groundwood mills sometimes carry chlorine residuals as high as 2 p.p.m. in the fresh water to obtain a bacteria-killing solution for washing equipment, washing felts, making up starch solutions, use in show-

³⁸ A. E. Griffin, *Paper Trade J.* 113, No. 9: 95-97 (Aug. 28, 1941)

³⁹ TAPPI Water Committee. "Industrial Water for Pulp, Paper and Paperboard Manufacture," TAPPI Monograph Series No. 1. New York (1942), 145 pp.

ers, etc. Excessive chlorine, however, leads to corrosion of equipment unless the pH of the water is maintained in the neighborhood of pH 6.0.

Use of Chloramine. To overcome the reactivity of chlorine with organic matter, chloramines have been used for treating mill stock. Because of the lower reactivity of chloramines, it is possible to maintain higher residuals than could be obtained from an equivalent amount of chlorine in the free state. Treatment with chloramine has been particularly effective with such pulps as groundwood, straw, and kraft, where there is a high concentration of lignin and other organic matter. Chloramines are not so well suited as chlorine for fresh water treatment.

In commercial chloramine treatment, the chlorine and ammonia are run into the mill system separately at a convenient point, such as the fan pump, white water return from deckers, or paper machine tray water. Special feeders are used to apply the two chemicals in the correct ratio, which is usually about 10 parts of chlorine to 1 part of ammonia. The dosage varies from about 1.0 lb. of chlorine and 0.1 lb. of ammonia to 3.0 lb. of chlorine and 0.3 lb. of ammonia per ton of pulp.

Chloramines have a lower oxidation potential, being only about one-twentieth to one-thirtieth as effective as chlorine in destroying coliform bacteria. However, chlorine is quickly dissipated, reaching its maximum efficiency in about 1.5 minutes,⁴⁰ whereas chloramine is effective over a much longer period of time. For example, by using 1 part of ammonia to 5 to 10 parts of chlorine, it is possible to slow down the reactions so that maximum activity is reached in about five to six hours.⁴⁰

Chloramines have decreased effectiveness at higher pH values. However, they are less affected by high pH values than chlorine, so that at pH values of 9.0 to 9.5, they kill faster than free chlorine residuals.⁴¹ However, neither agent is really effective at these high pH values.

Use of Chlorinated Phenols. Within recent years, several effective toxicants have been developed. One of the most successful of these has been the polychlorophenols. These are used in two forms, as the water-insoluble phenols and as the water-soluble sodium salts. These substances are highly toxic to bacteria, fungi, and algae, and have been successful in eliminating even the most resistant residual microorganisms.⁴²

The polychlorophenols have several advantages over chlorine. For one thing, they are not consumed by organic matter like chlorine and hence can be added directly to the paper mill system with good results. Another advantage over chlorine is that they are particularly effective against fungi; so much so, in fact, that they may be regarded essentially as fungicides.

⁴⁰ L. J. Rampel, *Paper Trade J.* 121, No. 22: 209-211 (Nov. 29, 1945)

⁴¹ N. S. Chamberlin and R. B. Martin, *Tappi* 32, No. 5: 215-220 (May, 1949)

⁴² J. R. Sanborn, *Paper Trade J.* 119, No. 25: 243-248 (Dec. 21, 1944)

They are also highly effective against certain of the sporeforming bacteria, such as *Bacillus subtilis*. On the other hand, they have the disadvantage of requiring a longer contact time for complete killing than chlorine. Also, they are not very effective for controlling the coliform bacteria, and hence are not well suited for fresh water treatment. *Oidium*, *Monilia*, and *Cladosporium* are other microorganisms which are difficult to control with chlorinated phenols. However, commercial chlorinated phenols differ widely in chemical composition and activity, and by selection of the proper combinations of materials it is possible to control practically all types of microorganisms.

Among the chlorinated phenols which are most widely used in the paper industry are orthophenylphenol, trichlorophenol (2,4,5, and 2,4,6), tetrachlorophenol (2,3,4,6), chloro-2-phenyl phenol, 2 chloro-4-phenylphenol, and pentachlorophenol. Usually the soluble sodium salts are used. Polychlorophenols are sold commercially in the form of prepared compounds containing anywhere from 20 to 90% active ingredient. Frequently, the compound contains alkalis which are added to increase the solubility and stability. In some cases, commercial compounds contain mixed fractions of active ingredients.

The sodium salt of pentachlorophenate is recommended for general use against fungi, and between 0.005 to 0.03% on the basis of the pulp is commonly used. The sodium salt of 2,3,4,6-tetrachlorophenol seems to be slightly better for use against bacteria, and as good as the pentachlorophenate for use against fungi. The 2-chlorophenylphenate is best for use against non-sporeforming bacteria, and is effective against more fungi than the other derivatives. The use of copper sulfate in combination with the chlorinated phenols is often advantageous, particularly for controlling *Oidium*, *Monilia* and *Cladosporium*.

In treating paper or paperboard for the prevention of mildew, soluble sodium pentachlorophenate can be added to the papermaking stock and precipitated on the fibers with acid or alum. The soluble salt is completely converted at a pH of about 6.8 into the relatively insoluble phenol derivative. Since the phenol derivative has a solubility in the neighborhood of 14 p.p.m. at 20° C., the retention is high, usually between 50 to 95%. The toxic efficiency is equivalent to that of the sodium salt from which it was formed,⁴³ and the vapor pressure is so low that 1% produces no odor in the paper at 100° F. and a relative humidity of 100%.

Appling and Shema⁴⁴ report that certain bacteria will develop a resistance to chlorinated phenols under laboratory conditions, so that they

⁴³ TAPPI Water Committee. "Industrial Water for Pulp, Paper and Paperboard Manufacture," TAPPI Monograph Series No. 1. New York (1942), 145 pp.

⁴⁴ J. W. Appling and B. F. Shema, *Paper Trade J.* 117, No. 14: 157-160 (Oct. 30, 1943)

can eventually grow in a medium containing as much as nine times the normal killing dosage. Their tests are interesting, since they illustrate the ability of microorganisms to adapt themselves to unfavorable conditions, but this situation is not generally experienced under practical conditions.

Use of Mercury Compounds. Another recent development has been the introduction of organic mercury compounds as paper mill toxicants. Mercury compounds are extremely effective in controlling both bacteria and fungi. They are less selective in their action but have a greater "knock-out" punch than the chlorinated phenols.

Among the mercury compounds in use at the present time are phenyl mercuric acetate (sold commercially as Merfenel, Mersolite, Bufen 30, and Puratized PMA); ethylmercuric phosphate (sold under the name of Lignasan); pyridylmercuric acetate (sold under the name of Pyridose); ethylmercuric chloride; phenylmercury borate; phenylmercury lactate (trade name Puratized SC); phenylmercury basic nitrate; and phenylmercury-monoethyl-ammonium acetate (sold under the trade name of Gallicide). One commercial compound (i.e., BSM-11) contains a mixture of alkali metal chlorophenates and phenylmercuric compounds. Another product (i.e., Butrol) contains a mixture of orthophenylphenates and phenylmercuric compounds. Commercial preparations such as Mersolite, Lignasan, Gallicide, BSM-11 and Butrol contain less than 100% active ingredient, since mercury compounds are not only quite expensive, but also highly effective toxicants and are safer to handle when diluted with inert materials. For example, BSM-11 contains 10% phenylmercuric acetate, 50% potassium 2, 4, 6 trichlorophenate and 40% solvent. About 5 to 25 p.p.m. of the commercial preparation (0.2–0.8 lb. per ton) generally are added, based on the weight of furnish passing through the system during the period of treatment.

Several precautions must be observed in the use of mercury compounds. For one thing, they are quite poisonous and should be handled with extreme care. Some of the dry products are packaged in small paper envelopes which are readily fiberized in water in order to prevent direct contact between the operating personnel and the active toxic material. All mercury compounds must, however, be used cautiously on paper surfaces which may come into contact with foodstuffs. Mercury compounds are quite expensive, and their use may involve the waste of considerable money unless properly applied. This does not necessarily mean that they should always be used in small concentrations, because too small dosages will not be effective. In addition, small dosages of mercury compounds actually stimulate the growth of some microorganisms,⁴⁵ although it should be pointed out that there is no mill case where this has happened. Organic

⁴⁵ J. A. Holmes, *Paper Trade J.* 113, No. 13: 164–166 (Sept. 25, 1941)

mercury compounds may be used very efficiently for the treatment of mill systems at special periods, such as just before a clean-up, and for the treatment of localized spots of infection.

According to Pehrson and Lindberg,⁴⁶ phenylmercuric acetate tends to be absorbed by pulp fibers in the absence of alum, but not absorbed to any extent in the presence of alum. Phenylmercuric acetate is completely sorbed when used in a groundwood pulp mill, but in the paper mill system a great part of the mercury compound circulates in the white water.⁴⁶ However, it has been shown that the adsorbed toxicant is biologically active. According to Wiltshire,⁴⁷ a minimum concentration of 1 p.p.m. should be maintained in the backwater for effective control.

Use of Other Toxicants. In addition to chlorine, chlorinated phenols, and organic mercury compounds, there are many other substances which can be used in paper mill systems to control microbiological activity. These include such substances as copper sulfate and potassium permanganate which are added primarily for their germicidal effect, and substances such as alum and zinc sulfide which are added for other reasons, but which have a slight inhibiting effect on certain microorganisms. Many of the bleaching agents also function as effective toxicants. Sodium salt of dihydroxydichlorodiphenylmethane (trade name Preventol GDC) is an example of a fungistat material which is non-toxic and non-irritant to humans.

Copper sulfate is quite toxic to algae and is frequently added to fresh water to prevent the formation of algae in settling basins and filters. The dosage is governed by the type of algae, but varies between 0.10 to 0.50 p.p.m. There is some evidence that copper sulfate is effective against the yeast type fungi and certain of the filamentous mold type fungi. However, copper sulfate is an inhibiting agent and not a killing agent. Furthermore, it is not very effective by itself, and seems to work best in combination with other toxicants which are stimulated by a trace of copper ion. Copper sulfate is very corrosive to machine parts, and this has limited its usefulness; but it is possible to use in the neighborhood of 10 lb. per 1,000,000 gal. without trouble.

Evaluation of Toxicants

The various toxicants in common use in the paper industry have been discussed, and something has been said about their relative efficiencies. However, new developments are constantly taking place, making it desirable that the paper chemist have a method of comparing toxicants for efficiency. This may be done either by the use of laboratory tests, or on the basis of mill trials.

⁴⁶ S. O. Pehrson and N. J. Lindberg, *Svensk Papperstidn.* 51, No. 19: 439-446 (Oct. 15, 1948)

⁴⁷ W. A. Wiltshire, *Paper-Maker*: 22-30, Midsummer Number (1948)

In the final analysis, mill records are the only absolutely reliable means for comparing toxicants. However, it may be necessary on occasion for the paper chemist to compare a series of different toxicants when it is not convenient or practical to try out a large number of unknown samples in the mill system. In such cases, laboratory methods may be used, and three possible methods are discussed below. However, it is important to remember that laboratory evaluation of slimicides is of value mainly in preliminary screening of chemicals for the purpose of separating the promising compounds from those that are ineffective. The only real and ultimate test of a slime control treatment is mill performance. It is a mistake to place too much emphasis on small-scale laboratory experimentation as a guide to dosages, points of application, or general effectiveness.

The first method, submitted by Sanborn, uses a special Petri dish with a porous porcelain top. This porous surface absorbs any condensate and prevents the spreading of toxicant except through the medium. The first step consists of pouring potato glucose agar medium (see plating) containing a suspension of a pure culture of a microorganism into several Petri dishes and allowing it to harden. Several different plates should be poured and these should include at least two sporeforming bacteria, a non-sporeforming bacterium, and several different molds. After the agar has hardened, a disk is cut out of the center of each plate, using a sterile cork borer, and then a definite amount [two to three drops] of toxicant are added to the hole (after first adding one to two drops of liquid agar to seal the bottom edges of the hole). The plate is then incubated without inverting, care being taken to see that the toxicant solution does not spill over the edges of the hole. The toxicant diffuses from the hole in the center into the medium and prevents growth of the microorganism in a clear zone about the center, the radius of which depends upon the vapor pressure, the diffusion coefficient, and the toxicity threshold of the toxicant. In order to determine whether the microorganism in the clear zone is killed or merely inhibited, it is necessary to take a small sample from this zone for incubating in some sterile broth. If growth results upon incubation, the organism is merely inhibited, but if no growth results, it is completely destroyed.

The second method of testing, also used by Sanborn, is a modification of the phenol test. In this test, test tubes containing 5 cc. of potato glucose broth are inoculated with different microorganisms. Young growths of bacteria and fungi are used for this inoculation, and these are obtained from potato glucose agar slants by adding 10 cc. of sterile water and a few sterile glass beads, and shaking for a few minutes to dislodge the microorganism, after which the suspension is transferred aseptically into 100 cc. of sterile water. After inoculation, the tubes are incubated for three to four hours at 32° F. At the end of this time, 0.5 cc. of toxicant solution at different

concentrations is added to each tube except the control. (It is convenient to use solutions containing parts of toxicant to parts of water of 1 to 100, 1 to 500, 1 to 1,000, 1 to 2,000, 1 to 5,000, and 1 to 10,000. When 0.5 cc. of these are added to the 5 cc. of broth, the concentrations of toxicant in the test sample then become respectively 1 to 1,000, 1 to 5,000, 1 to 10,000, 1 to 20,000, 1 to 50,000 and 1 to 100,000.) The cultures are finally incubated for the second time (48 hours in the case of the bacteria, and 3 to 7 days for the fungi) and then examined for growth as evidenced by cloudiness, surface scum, or a sediment in the bottom of the tube. As a final step, it is informative to make sub-cultures of those samples showing no growth in order to determine whether the microorganism is merely inhibited or actually killed. By this method of testing, a good toxicant should control growth at a ratio of less than 1 part of toxicant to 10,000 parts of water. Anything which requires a higher concentration than this may be considered relatively ineffective. Sartoretto^{47a} points out that best results are obtained with this test when mixed slimes taken from the paper mill are used in place of pure cultures.

The third method of testing is an important modification of the second method, which has been introduced by King⁴⁸ and subsequently modified by Appling and coworkers.⁴⁹ In this method, paper mill slurry (or white water sludge) is used as the medium during the contact period between test organism and toxicant. In making the test, 100-cc. samples of fresh mill water are pipetted into 250-cc. Erlenmeyer flasks. From each flask a volume, equal to that of the toxicant solution to be added, is removed aseptically. The desired amounts of toxicant are then added aseptically to the various flasks, bringing the total volumes back to 100 cc. Each flask is rotated immediately to mix the toxicant thoroughly with the water. The flasks are then incubated at approximately the temperature of the mill system from which the slurry (or white water sludge) was taken. After six hours of incubation at the selected temperature, a 1-ml. sample from each flask is plated on nutrient agar. The initial bacterial count is determined by plating from a flask containing no toxicant. After forty-eight hours at 37° C., the plates are counted. Table II summarizes the data obtained when four toxicants were compared by this method.⁴⁹

In order to apply data of this sort to a mill system, Appling and coworkers⁴⁹ arbitrarily decided to select as the probable minimum effective dosage that which caused a reduction of 99% in bacterial count after six hours of contact or, in other words, when survival was only 1% of the initial population. Referring to Table II, Lignasan applied to a white water

^{47a} P. A. Sartoretto, *Tappi* 34, No. 1: 72A-73A (Jan., 1951)

⁴⁸ G. King, *Pulp Paper Ind.* 18, No. 6: 39-42, 44, 46 (June, 1944)

⁴⁹ J. W. Appling, J. F. McCoy and B. F. Shema, *Paper Trade J.* 124, No. 22: 143-154 (May 29, 1947)

TABLE II

COMPARISON OF TOXICANTS USING MILL WATER AS THE MEDIUM

Mill sample	Disinfectant	Time, hr.	Counts per ml. at dosage indicated, p.p.m.							
			0	0.5	1.0	2.0	4.0	6.0	8.0	10.0
1. White water sludge	Lignasan	0	17,000,000
(groundwood pulp mill No. 1) ...		6	32,100,000	13,800,000	4,500,000	840,000	79,000	33,000	24,000	14,000
2. White water	Lignasan	0	0	5.0	10.0	15.0	20.0	25.0
(groundwood pulp mill No. 2) ...		6	1,430,000
			7,500,000	5,400,000	3,000,000	640,000	72,000	31,000
3. White water sludge	Merfenelope	0	0	0.2	0.4	0.6	0.8	1.0
(groundwood pulp mill No. 1) ...		6	17,000,000
			32,100,000	10,200,000	11,400,000	5,100,000	3,700,000	3,570,000
4. White water sludge	Pyridose	0	0	0.2	0.4	0.6	0.8	1.0
(groundwood pulp mill No. 1) ...		6	17,000,000
			32,100,000	5,600,000	1,100,000	310,000	56,000	39,000
5. Groundwood slurry 1%	Pyridose	0	0	0.1	0.2	0.4	0.6	0.8	1.0	2.0
(groundwood pulp mill No. 1) ...		6	6,000,000	15,100,000	10,800,000	2,610,000	192,000	43,000	125,000	2,000
			13,700,000
6. Filler slurry	Pyridose	0	0	0.01	0.1	1.0	10.0
(board mill)		6	62,000,000	170,000,000	156,000,000	36,000,000	380,000
			0	25	50	75	100	150	200	250
7. White water	Santobrite	0	522,000
(groundwood pulp mill No. 2) ...			540,000	430,000	110,000	85,000	30,000	14,300	6,300	5,000

sludge sample from groundwood pulp mill No. 1 was effective at a dosage level of 2 p.p.m. in producing a 95% kill and at a level of 4 p.p.m. in producing a 99.5% kill. One can readily locate this level by observing where the 1% survival figure falls (1% of initial count or 170,000). Since this falls between 2 and 4 p.p.m., the probable minimum effective dosage for Lignasan in the system, from which the white water sludge was taken, is greater than 2 but less than 4 p.p.m. Obviously, this method depends upon the microflora in a particular sample and the toxicant adsorbing capacity, as well as upon the ability of the toxicant to kill microorganisms. In practice, this method has given excellent results for various paper and pulp mill systems.

All laboratory evaluations have one common deficiency, namely, that they fail to indicate whether or not the dosage of toxicant recommended is definitely related to slime control. Several mills have sought to improve on these methods by the introduction of surfaces for slime deposition which can be removed from the system periodically for inspection. As previously mentioned, slime-measuring units made from panels of pine, oak, rubber, or cement have been devised,⁵⁰ and at the present time, these measuring units offer a positive and effective means for correlating toxicant dosage with slime control. Slime boards are useful in following the course of treatment with toxicant, in determining the effectiveness of control, and for indicating the adjustment of toxicant required to suit prevailing conditions. Control is considered to be generally effective if not over 50 mg. of dried slime, 18 to 20 g. of wet weight, are removed per square foot per day,⁵¹ although this depends upon the grade of paper being made. Recent reports⁵² indicate that the rate of accretion in grams of wet slime per 1,000 sq. cm. per twenty-four hours should be no greater than 10 to 20 g. for newsprint, kraft papers, and folding box-boards, and no more than 5 to 10 g. for fine papers. Considerable judgment, based upon past experience, is required to judge the significance of the readings in terms of rate of build-up of slime. The physical characteristics of the panel slime growth are important. New slime boards must be immersed for several weeks to several months before they will grow slime satisfactorily. Daily sterilization of slime boards is advocated by some. This reduces the rate of accretion, and it is claimed that the results obtained are a truer index of slime growth in the paper mill system than those obtained with unsterilized boards, although this is a controversial point.

One factor to be considered in the testing of toxicants is that mixtures of toxicants are sometimes more effective than any one toxicant used alone.

⁵⁰ F. S. McCall and R. T. Hudson, *Paper Ind.* 29, No. 10: 1502-1504 (1948)

⁵¹ W. N. McKee, *Paper Mill News* 73, No. 11: 12-23 (Mar. 18, 1950)

⁵² Report in Paper by W. D. Stitt, *Tappi* 33, No. 6: 74A-75A (June, 1950)

This is known as synergism. For example, 2,4,5-trichlorophenol is ineffective in controlling bacteria, and copper sulfate by itself has no effect at all, but in combination they are highly effective. Typical results are shown below :

Toxicant	Effective dilution (Method 2)
2,4,5-Trichlorophenate	1 to 1,000
Copper sulfate	0
2,4,5-Trichlorophenate plus copper sulfate	1 to 100,000

Mercury ion also has this synergistic (stimulating) effect, and sometimes magnesium ion, although to a lesser extent. Mercurials and chlorinated phenates are compatible in low concentrations. Extra alkali is helpful in increasing compatibility.

The pH is another important factor in toxicity measurements since the effectiveness of a given toxicant depends upon the pH. For example, Appling and coworkers⁵³ found phenylmercuric acetate to be most effective against *Aerobacter aerogenes* and *Bacillus mycoides* at a pH of 7, whereas it was most effective against the mold type fungi at a pH of 8.5. They found the effectiveness of the pentachlorophenates to be even more dependent upon pH.

In conclusion, it should be emphasized that there are many factors involved and that it requires considerable experience and good judgment to choose the proper toxicant for the conditions at hand. Snap judgments should not be made, since some toxicants require a considerable period of time to make themselves felt. It sometimes happens that a new toxicant, when first added to the system, causes a temporary increase in slime spots in the paper. These are caused by slime breaking loose in the system, and in such cases, the situation will generally clear up in a few days. In a few cases, toxicants have actually increased microbiological activity. This is sometimes hard to explain, but generally it is the result of a killing off of some of the principal types which gives other types a better chance to grow. In these cases, another toxicant which is effective against the secondary organisms will result in a complete suppression of growth.

Microbiological Requirements of Paper and Paperboard

Mold or mildew, which is the layman's term for excessive growth of filamentous fungi, sometimes appears on the surface of paper, provided there is sufficient air, moisture, and ample foodstuff available. Mildew on paper and paperboard products is undesirable, since it is unsightly, con-

⁵³ J. W. Appling, J. F. McCoy and B. F. Shema, *Paper Trade J.* 124, No. 22: 239-250 (May 29, 1947)

taminates other materials, weakens the paper, and produces bad odors. If present in the pulp supply, it furnishes a source of contamination to the mill system. The common filamentous molds which produce mildew belong to such genera as *Penicillium*, *Aspergillus*, *Mucor*, and *Rhizopus*.

Under normal conditions, paper is not a good medium for the growth of molds. Paper contains an abundance of food substance, but this food is not readily available because of the low moisture content and because most of the water is held by the fibers. The presence of fermentable substances such as starch, casein, glue, and plasticizers in the paper does not mean that the paper will mold, because here again, the moisture content of the paper is usually so low that no growth takes place under normal conditions. In fact, Frieden⁵⁴ points out, in some cases, at least, that the presence of starch in paper reduces molding because the starch binds the water picked up from the atmosphere before it can be utilized by the microorganisms.

Paper and paperboard are sometimes used and stored at high moisture content so that mold growth is favored. Paper containers used for the cold storage of eggs, where the humidity must be kept high to prevent loss of water from the eggs, and paper soap wrappers, which pick up moisture from the soap, are very likely to mold. In cases of this kind, the presence of fermentable materials in the form of special coatings, plasticizers, adhesives, or sizing agents will increase the molding tendency of the paper. The presence of urea-formaldehyde resins in paper tends to retard the growth of mildew.⁵⁵ However, wet-strength papers which come into contact with wet earth or other places where microorganisms are prevalent lose their wet strength fairly rapidly, due probably to attack on the cellulose.⁵⁶

Mildew also appears on wet-lap pulp or on waste papers which are stored in damp places. The growth of microorganisms in wet groundwood lap pulp (50% moisture) results in a substantial loss of fiber by decay, staining, etc. However, there appears to be a tendency for the bacteria in stored groundwood pulp to reach a maximum and then decrease, possibly due to exhaustion of the food supply or to generation of toxic substances by the bacteria themselves.⁵⁷ Gadd⁵⁸ points out that mold fungi do little damage to wet groundwood lap pulp, but that rot fungi (*Lentinus*, *Lenzites*, *Paxillus*, *Pholiota*, *Peniophora*, *Stereum*, *Polystictus*, and *Corticium*) cause considerable decomposition if the pulp is left for an appreciable length of time. The extent of rot decay can be estimated by staining the pulp with Congo red or brown-cresol-green to detect the presence of acid. It has been

⁵⁴ A. Frieden, *Paper Trade J.* 110, No. 17: 233-236 (Apr. 25, 1940)

⁵⁵ W. I. White and R. G. H. Siu, *Ind. Eng. Chem.* 39, No. 12: 1628-1630 (Dec. 1947)

⁵⁶ C. S. Maxwell and W. F. Reynolds, *Tappi* 33, No. 4: 179-182 (Apr., 1950)

⁵⁷ J. S. Reichert, R. T. Mills and D. J. Campbell, *Paper Trade J.* 122, No. 5: 41-43 (Jan. 31, 1946)

⁵⁸ G. O. Gadd, *Pulp Paper Mag. Canada* 50, No. 11: 98-99 (Oct., 1949)

shown that wet groundwood lap stock can be controlled for a storage period of one year by treatment with about 0.5 lb. of a 10% solution of phenylmercuric acetate per 2,000 lb. of pulp when the toxicant is added to the white water system.⁵⁹

There are several methods by which paper and paperboard may be treated with toxicant to prevent mildew. One method consists of adding toxicant to the furnish in such a way that it is carried through to the finished paper. This method can sometimes be used with the chlorinated phenols, whereby the soluble sodium salt (about 15 to 30 lb. per ton⁶⁰) is added at the beater and then precipitated with alum (*pH* about 4.5) so that the insoluble pentachlorophenol is adsorbed on the fibers. Beater addition is, however, not so effective as surface addition.

With coated or surface-treated papers, toxicants may be added directly to the coating or sizing mixture. Toxicants are available for incorporating in lacquers, waxes, asphalts, starches, etc., and when added in this way, the toxicant is present in highest concentration on the surface of the paper where it is most needed. Some of the resins and plasticizers used in lacquers are inherently mold-resistant and hence impart mold resistance to the coated paper. The phenolics, polyethylene, methacrylates, polyvinyl chloride-acetate, and polystyrene are some of the resins which are mold-resistant; chlorinated diphenyls, phosphates, and phthalic acid derivatives are some of the plasticizers which are mold-resistant.

Another method of producing a mold-resistant surface involves the application of toxicant solution to the surface of paperboard at the calender stacks, using about 2.5 to 5.0 lb. of chlorinated phenol or 0.3 to 0.6 lb. of organomercurial per side per ton of board. Supplementary beater treatment is generally recommended with the chlorinated phenols. If the toxicant is used in surface coatings for food containers, toxicants which are relatively odorless and relatively non-toxic are safest. Sodium propionate (trade name Mycoban) and calcium propionate are non-toxic to humans, and have been used in food wrappers and even in the food product itself. Alkyldimethylbenzylammonium chloride (trade name Roccal) and sodium salt of dihydroxydichlorodiphenylmethane (trade name Preventol GDC) are other suitable non-toxic materials. Diphenyl is sometimes used in paper wrappers for oranges to keep down mold.

A method sometimes used with corrugated or laminated paperboard is to incorporate the toxicant with the adhesive. In this application, the toxicant protects the adhesive from spoilage during use and also protects

⁵⁹ S. J. Buckman, *Tappi* 32, No. 3: 127-144 (Mar., 1949)

⁶⁰ This, as well as other dosages given, are only approximate values. Recommended dosages have varied considerably through the years for a number of reasons, and hence the reader is referred to manufacturers of toxicants.

the adhesive film in the final laminated product. Ordinarily, little or no protection is furnished to the surface of the board, although it has been claimed that sodium pentachlorophenate diffuses through the board and produces a mold-resistant surface.⁶¹ This effect appears to be more pronounced with silicate-laminated paperboard than with starch-combined board.

• There are several methods for evaluating the fungicidal and bactericidal properties of treated paper or paperboard. One laboratory method consists of placing a 2-in. square of the paper to be tested on the surface of a special agar medium which has hardened in a Petri dish.⁶² To the surface of this paper is then added a small amount of a suitable organism such as *Chaetomium globosum*, *Aspergillus niger*, etc., in the form of a dilute suspension containing disintegrated filter paper and salt. Another method⁶³ eliminates the agar but retains the other features of this method. The test specimen is wetted with mineral salts medium and inoculated, as in the preceding case. The dishes are closed with rubber seals. The treated sample is incubated for one to three weeks, and the amount of growth is noted visually. Another method⁶⁴ consists of placing an inoculum of *Chaetomium globosum* in a cutout from the center of a specimen of paperboard, after which the treated sample is then sandwiched between two untreated samples of paperboard. The time and extent of growth are then noted after a definite incubation period.

Microorganisms in Non-Fibrous Materials

Aside from the microbiological problems connected with pulp and paper mill systems, the paper mill chemist is also interested in the microbiology of non-fibrous raw materials. Starch, animal glue, and casein are three widely used materials which are subject to fermentation or decomposition. Other fermentable materials used in the paper mill are technical gelatin, vegetable gums, soy flour, soybean protein, some plasticizers, wax emulsions, and other similar materials. All these materials are subject to spoilage unless properly used or protected by means of a preservative.

Spoilage of non-fibrous materials must be avoided for the same reasons it should be avoided in the paper mill system. Spoilage means economic loss. A spoiled batch of casein or starch must be run to the sewer, as otherwise it will cause trouble in one or more of the following ways: loss in viscosity, loss in adhesiveness, excessive foaming, bad odor, and change in pH.

⁶¹ D. K. Ballman and F. B. Smith, *Paper Ind.* 25, No. 2: 143-149 (May, 1943)

⁶² B. F. Shema, *Paper Trade J.* 123, No. 23: 179-180 (Dec. 5, 1946)

⁶³ J. W. Appling, S. J. Buckman and C. D. Cash, *Tappi* 32, No. 9: 427-429 (Sept., 1949)

⁶⁴ B. F. Shema, *Paper Trade J.* 127, No. 26: 536-537 (Dec. 23, 1948)

Starch

Starch is a fermentable substance and, as such, must be used with proper care to prevent the unrestricted growth of microorganisms. Most commercial starches contain large numbers of bacteria and other organisms. Tapioca starch generally contains more microorganisms than corn starch, and the unmodified starches generally contain more microorganisms than the modified starches, inasmuch as the chemicals used in modification tend to destroy all living organisms. As a rule, modified starches (oxidized starches, dextrins, etc.) contain few microorganisms when received at the mill, and practically never contain pathogenic organisms or associative types such as *Escherichia coli*. However, there is always the possibility that the starch has been contaminated in shipping, and the paper chemist should never depend upon any type of starch being entirely free of microorganisms.

Even though heavily contaminated with microorganisms, starch will never spoil in the dry state and, as a matter of fact, there is a tendency toward a reduction in the number of bacteria on standing. However, starch which is stored at high moisture content or in damp places will tend to mold. Cooked starch solutions are fermented by many microorganisms commonly occurring in soil, air, and water, but even so, starch solutions do not spoil so readily as the proteins, and most starch solutions used in the paper industry will hold for two to three days without spoilage, unless they are heavily contaminated. The highly modified dextrins spoil more readily than unmodified starches, apparently because of the higher percentage of sugars and soluble food substances which they contain.

Starch solutions develop a bad odor on spoiling, but in the early stages of spoilage, very little, if any, odor is produced. The presence of gas bubbles in starch solutions is another manifestation of spoilage, but gas bubbles, too, are not apparent until spoilage is well advanced. Hence, the paper chemist should never wait until these warnings appear before applying corrective measures, because the starch is too badly spoiled to be of any use by that time. Significant changes in the properties of the starch due to spoilage can occur before there is any appreciable amount of odor or gas. In one case involving the use of starch for surface sizing, the sizing fell off nearly 25%, and in another case involving the use of starch for pigment coating, the bonding strength was greatly reduced; but the operators did not recognize that this was due to spoilage because there was no bad odor. When toxicants were applied to subsequent batches, spoilage was stopped and the starch returned to its original strength. A slight loss in viscosity or sizing value may be regarded as a more sensitive indication of spoilage than either odor or gas production.

Starch is almost always cooked to 90° C. or above before use, and this eliminates all microbiological life except the thermophilic bacteria. These

heat-resistant bacteria cannot be controlled except by chemical means. Some starch companies manufacture thermophile-free starches, but these are used principally in the canning and food-processing industries, and are almost never requested by the paper industry. The use of preservatives with starch is discussed in a later section.

Proteins

Proteins are subject to decomposition by a large variety of microorganisms. The process is called putrefaction and is evidenced by the development of bad odors and gas formation resulting from the general breakdown of the protein molecule. Animal glue, casein, soybean protein, albumen, and all other proteins are subject to putrefaction if conditions are favorable for microbiological growth.

The undesirable effects resulting from putrefaction of proteins are much the same as those just described for the fermentation of starch. Poor sizing, excessive foaming, and bad odors are several of the difficulties which can often be traced to spoilage. In pigment coating, spoilage of the casein results in a reduction in viscosity and a loss in pigment bonding strength. In the preparation of albumen plates for halftone printing, it is common practice to prepare the albumen on the night before, and unless a preservative is added, spoilage occurs, resulting in a loss in viscosity. This causes poor coverage of the plate and may lead to scumming during printing.⁶⁵ Spoilage also causes the cast film to be opaque, which prevents light from penetrating through the whole thickness of the film during exposure.⁶⁵

Control Measures

Cleanliness is the most important single factor in the handling of sizing agents, adhesives, coatings, and similar organic materials which are liable to spoilage. The tank in which the material is prepared should be thoroughly cleaned after each use by washing with hot water and, on occasion, by soaking overnight with a germicidal solution. The latter precaution should be followed where wooden tanks are used, inasmuch as wood tends to hold microorganisms within its pores.

Many mills do not use preservatives in the preparation of starch and protein sizing agents. In most cases, this procedure is satisfactory, since the material is used within a very short time, and any microorganisms present do not have a chance to develop. The use of a preservative is safer, however, and is a wise precaution in cases where the size is to be kept for several days. Preservative should always be used if the material is stored warm.

The number of preservatives is large, and some are more effective than

⁶⁵ H. A. Beechem, *Modern Lithography*, p. 34 (July, 1942)

others. Among those which have been used are zinc salts, copper salts, fluorides, chlorine, hypochlorite, chlorinated phenols, boric acid, borax, benzoic acid, benzoates, salicylic acid, salicylates, organomercurials, phenol compounds, formaldehyde, and alum. A new type of commercial preservative is the betahydroxyethylpyridinium salt of 2-mercaptobenzothiazole (sold under the trade name of Vancide 32). This is a water-soluble and non-toxic material with a slight pyridine-like odor, and is reputed to be quite effective against fungi.

Formaldehyde and paraformaldehyde are good preservatives for starch, being particularly effective against bacteria. Formaldehyde is also effective with proteins, but it must be used with caution, since it is likely to cause gelling and brittle films. Copper salts work well in starch solutions, particularly in combination with formaldehyde. Sodium pentachlorophenate is effective with starch, but casein can be treated most effectively with the 2,4,5-trichlorophenate.⁶⁶ Table III compares the effectiveness of different

TABLE III
PRESERVATIVES FOR STARCH

Preservative	Amount	Period of holding
Paraformaldehyde	0.5%	30 days or more
Copper sulfate	0.5%	28 days
Fluorides	1.5%	4 days
Borax		Ineffective
Sodium benzoate or benzoic acid	0.2%	14 to 21 days
Salicylic acid	Less effective than benzoic acid	
Phenol	Requires 4%	
Zinc salts	1.5%	15 days
Sodium silicofluoride	1.5%	13 days

preservatives with starch, the amount given being the percentage of preservative based on the weight of dry starch necessary to prevent spoilage during the period of holding.⁶⁷ The preservation of soy flour mixtures is an ex-

TABLE IV
PRESERVATIVES FOR SOY FLOUR

- 2% chlor symmetrical xlenol
- 5% sodium pentachlorophenate
- 2% formalin (added to clay)
- 8% pine oil (volume basis)
- 2% 4-tert-butyl-m-cresol
- 1/2% copper sulfate and 1/2% quinolinol phosphate

⁶⁶ D. K. Ballman and F. B. Smith, *Paper Ind.* 25, No. 2: 143-149 (May, 1943)
⁶⁷ A. Frieden, *Paper Trade J.* 110, No. 17: 233-236 (Apr. 25, 1940)

ceedingly difficult proposition. Some of the most effective preservatives for soy flour dispersed with 6 to 7% sodium hydroxide and used in pigment coatings for wallpaper are given in Table IV. The percentage of preservative is based on the weight of dry soy flour and is the minimum amount necessary to preserve for several days a coating made with 100 parts clay, 12 parts soy flour, and 150 parts water.

The following proportions of commercial sodium pentachlorophenate preparation are recommended by the manufacturer for preserving different materials.

Types of material	Per cent toxicant
Corn starch	0.125 to 0.500
Dextrins	1.0
Casein (dispersed in ammonia)	1.0 to 2.0
Casein (dispersed in borax)	0.3 to 0.6
Soy protein	1.0 or more
Glue	0.25 to 0.50
Blood albumen	2.0 or more

Biochemical Oxygen Demand of Mill Waste Waters

Fresh water supports many complex biochemical processes, among which are those which arise from the life functions of fish, plant, and lower forms of life. In order to support these processes, a certain minimum amount of dissolved oxygen (D.O.) is necessary. It is generally agreed that water should have a minimum of 2 to 3 p.p.m. of dissolved oxygen to maintain normal growth of game fish and microbiological life. If the oxygen content falls much below this value, a septic condition results (due to organisms utilizing oxygen from other sources, such as that in sulfates) causing the evolution of odors.

All uncontaminated water in streams and lakes maintains the minimum oxygen content. However, water contaminated with organic matter tends to use up dissolved oxygen in the oxidation of the organic matter. In other words, the foreign matter has an oxygen demand which upsets the oxygen balance of the stream, and if sufficiently great, leads to the destruction of fish and plant life. Often the D.O. of water many miles below a paper mill is below the minimum necessary to support plant and fish life. Since time is required for the oxygen demand to develop, the greatest depletion of oxygen occurs at some point downstream from the mill site, at a distance equivalent to four or five days' flow.⁶⁸

Increasing competition for the use of available waters for disposal of mill wastes has made it necessary to conduct studies on the ability of streams to carry wastes without impairing the use of the stream for other purposes. The trend toward stiffening legislation covering the pollution

⁶⁸ J. P. Tully, Forest Products Research Society Bulletin 57. 12 pp. 1949 reprint.

of state, interstate, and national bodies of water has made the subject of stream pollution of increasing concern to the paper industry. So far, there has been considerable confusion, but the combined efforts of mill, government, and advisory bodies have resulted in many improvements, although much still remains to be done. Regulations are based upon stream hydrology, that is, stream flow and frequency and severity of droughts, as well as a knowledge of the pollutorial load of different mill wastes. In making studies, four sampling stations should be set up: (1) at the stream above the waste discharge, (2) at the point of waste discharge, (3) and (4) at two points downstream.⁶⁹ By suitable analysis, it is possible to compute the biochemical oxygen demand (B.O.D.) of the plant waste which the stream can accept without excessive oxygen depletion of the stream. The B.O.D. gives information on the oxygen depleting potentials of mill wastes in natural streams.

Measurement of B.O.D.

The biochemical oxygen demand (B.O.D.) is an arbitrary indication of the amount of organic matter present in waste water obtained by measuring the amount of dissolved oxygen consumed in the oxidation of the organic matter in the water to a stable state, using a mixed population of organisms under certain specified conditions. The amount of dissolved oxygen is measured on suitably prepared samples before and after incubation, using 0.0125 *N* sodium thiosulfate, 1 ml. of which is equivalent to 0.1 mg. of dissolved oxygen. The results are reported as biochemical oxygen demand in p.p.m. for the waste material. The test involves many techniques with which the paper chemist may not be familiar, and hence the reader is referred to standard books on the subject.^{70, 71} Results vary rather widely, depending on the conditions of the test, and consequently a sufficient number of samples should be tested to give a statistically acceptable average.

In making B.O.D. measurements, the test sample is diluted with a standard quantity of stored aerated river water or stabilized distilled water containing fixed amounts of minerals, nitrogen, and phosphorus. The sample is seeded to insure a sufficiently large supply of microorganisms to promote a normal rate of decomposition of the organic matter in the water. The seeding material is generally fresh settled (unfiltered) domestic sewage or soil extract. The concentration of sample should be chosen to obtain oxygen depletions within the range of 25 to 75%. The final B.O.D. may, in some cases, be calculated to a 50% oxygen depletion on the principle that

⁶⁹ F. W. Kittrell, *Tappi* 32, No. 12: 540-542 (Dec., 1949)

⁷⁰ D. Paul Rogers, *Tappi* 32, No. 11: 481-488 (Nov., 1947)

⁷¹ American Public Health Assoc., "Standard Methods for the Examination of Water and Sewage," 9th ed., Lancaster, Pennsylvania, Lancaster Press, Inc. (1946)

the growth is at a maximum at about this point. Rogers⁷⁰ recommends the following concentrations as starting points: mixed pulp and paper mill wastes, 0.1 to 1.0% ; sulfite waste liquor, 0.01 to 0.1%. Concentration factors are used to convert the results of B.O.D. to a concentration of 100%.

The temperature of incubation is usually maintained at 20° C. The period of incubation is standardized at five days, since the primary reaction is generally complete in this time, and in this period of time, most waste has reached a large body of water and is greatly diluted. The pH and temperature of incubation must be such that biological activity is free and unrestricted during the test period. All glassware should be thoroughly cleaned and all air bubbles eliminated from the apparatus. Special care must be taken to eliminate all materials from the sample which destroy microorganisms, e.g., copper ion, alkali, acids, or toxicants. Toxicants of the chlorinated phenol or organic mercury types cannot be destroyed, but the samples should be diluted to the point where their effect on the activity of the microorganisms is not significant. Phenols must not be in excess of 4.0 p.p.m., and copper salts in excess of 0.1 p.p.m.⁷⁰

B.O.D. should be a measure of the oxygen utilized by microorganisms only. Certain inorganic substances, e.g., sulfur dioxide found in waste sulfite liquor, consume oxygen and increase the oxygen demand. These materials, as a rule, consume oxygen very rapidly, and hence it is desirable to measure their oxygen demand as distinct from the B.O.D. Correction factors should thus be applied for the immediate oxygen demand, due to chemical oxidation of dissolved materials.

When volumes of flow of waste liquor are known, it is convenient to express B.O.D. in parts per million of waste liquor. If volume of flow is not known, the B.O.D. is commonly expressed in terms of population equivalent per ton of product produced. A population equivalent is the five-day oxygen demand of the waste discharged daily by one person, and has been established at 0.167 lb. of B.O.D. per day. Another value sometimes used in reporting on mill wastes is the pounds of suspended solids per ton of product.

Because of the length of time required to determine the five-day B.O.D., attempts have been made to develop more rapid methods based upon the amount of oxygen consumed from permanganate, potassium dichromate, or other oxidizing agents. These chemical methods do not differentiate between biologically stable and biologically unstable forms of organic matter, but the results seem to correlate fairly well with B.O.D. obtained by conventional methods on pulp and paper mill waste.^{71a}

^{71a} K. G. Chesley, R. W. White and R. V. Hogg, *Tappi* 34, No. 2: 87-88 (Feb., 1951)

Comparison of Different Mill Wastes

Mill wastes vary widely in the effect which they have on stream pollution. Rudolfs and Axe classify mill wastes as follows:⁷² These results apply only to wastes from news and chipboard mills, and it should be pointed out that the strength of most paper mill wastes runs considerably lower than these values.

Classification	Suspended matter, p.p.m.	B.O.D., p.p.m.
Strong waste	400 and over	400 and over
Medium waste	200-400	150-300
Weak waste	100-200	100-150

Values of B.O.D. for various mill wastes suggested by the National Council for Stream Improvement as representing reasonably good operation for mills located in one of the large eastern states are given in Table V.

Sulfite waste liquor presents a greater pollution problem than sulfate or soda mill waste liquor because of the high biochemical oxygen demand. The principal offending substances are dissolved materials such as carbohydrates

TABLE V

VALUES OF B.O.D. FOR VARIOUS MILL WASTES REPRESENTING
REASONABLY GOOD OPERATION

Source of waste	Population equivalent per ton of product	Pounds of suspended solids per ton of product
Sulfite pulp mill	3000-4000	35-45
Alkaline pulp mill	200-300	40-60
Groundwood mill	100-130	70-85
Deinking plant	200-800	600-1100
Rag plant	800-850	250-300
Bleaching plant	100-200	35-45
Paper mill	10-100	100-125

(e.g., pentosans), salts (e.g., sodium acetate), and soaps, such as soluble fatty acid soaps. Lignosulfonic acids are not particularly harmful, since they undergo relatively little decomposition in mill streams.⁷³ Soda and sulfate pulp mill wastes have a relatively low oxygen demand, because most of the soluble organic material in the waste liquor is burned in the alkali recovery process. The weak wash liquors from sulfate and soda pulp mills which escape the recovery process have a toxic effect on fish and plankton, because of the chemicals in the liquor (for example, sodium hydroxide, sodium carbonate, sodium sulfide, soap, methyl mercaptan, and hydrogen sul-

⁷² W. Rudolfs and E. J. Axe, *Paper Trade J.* 126, No. 14: 37-42 (Apr. 1, 1948)

⁷³ Annual Report, National Council for Stream Improvement, *Paper Trade J.* 130, No. 1: 22-28, 40 (Mar. 16, 1950)

fide), but with efficient recovery, the concentrations of these materials are so low by the time the wastes are diluted at the receiving stream that there is no hazard to fish or other aquatic life.⁷⁴ Waste from deinking plants and mills using the semichemical process is quite harmful because of the large amount of suspended solids, strong odor, and high B.O.D. of the liquid fraction. However, wastes from these sources have a lower biochemical oxygen demand than sulfite waste liquor because of the smaller amount of carbohydrate material carried, which is the primary cause of B.O.D. Ordinarily, deinking plant waste contains 570 to 3,072 p.p.m. of suspended matter, turbidities from 1,000 to 3,200 p.p.m., and B.O.D. from 345 to 1,135 p.p.m.⁷⁵

Paper mill wastes have an unfavorable influence on the D.O. content of mill streams, since they contain high proportions of organic substances such as fiber, starch, gums, and dyestuffs. Certain of the solid matter is in the dissolved state, but a considerable portion of the matter is in the suspended state, e.g., fibers, and this must be liquefied prior to oxidation. Considerable time is involved in the complete oxidation of the suspended matter, but even fibers exert some effect on the five-day B.O.D.⁷⁶ Some paper mill wastes contain excessive amounts of acid (e.g., mills making parchment), toxicants, and other similar materials which do not lower the B.O.D. but do other damage to the stream.

Methods of Treating Mill Waste

Some of the methods suggested for reducing the B.O.D. of mill wastes prior to entry into near-by streams are: chemical treatment of the waste by lime precipitation or alum coagulation, storage of the waste in lagoons, aerobic and anaerobic digestion of the waste, and aerobic oxidation of the waste.

Paper and pulp mill wastes can be partially clarified by settling, flocculation, and filtration before going to the sewer, and to date these are the only methods used to any extent. In general, these processes can be carried out in a manner similar to the treatment of fresh water, with the difference that the waste water contains a much greater amount of solid matter, and consequently requires greater treatment than fresh water. The treatment of paper mill white water is discussed in the section on the reuse of white water in Chapter VIII.

Conventional methods of coagulation and sedimentation do not greatly reduce the B.O.D. of waste water, because most of the oxygen demand is due to soluble matter in the water.

⁷⁴ W. M. Van Horn, J. B. Anderson and M. Katz, *Tappi* 33, No. 5: 209-212 (May, 1950)

⁷⁵ P. F. Morgan, *Paper Trade J.* 126, No. 20: 237-241 (May 13, 1948)

⁷⁶ H. W. Gehm, *Tappi* 33, No. 3: 124-126 (Mar., 1950)

Aeration of the waste during storage accelerates the B.O.D. removal and reduces the load on the stream. By treating total kraft mill waste with as little as 0.5 cu.ft. of air per gallon of waste per day, it is possible to reduce storage time to one-sixth of that required without aeration.⁷⁷ The addition of salts containing nitrogen (e.g., nitrates and ammonia) is beneficial in accelerating decomposition of the organic matter. Recently, experiments have been conducted along the line of increased aeration and treatment of the waste with non-pathogenic seed organisms obtained from domestic sewage. The waste is constantly aerated during treatment and sodium nitrate and phosphorous salts added to the extent of about 12 p.p.m. After the waste liquor is aerated and fully treated, it is passed into a final sedimentation tank where the biological sludge is settled. The sludge can be pumped back to the inlet of the aeration tank for recycling. The treated waste liquor can be run directly from the sedimentation tank to the river. Experimental work indicates that it is possible, by this method, to remove from 65 to 85% of the objectionable organic material and lower the B.O.D. accordingly.

One suggested method of handling paper mill wastes is in trickling filters by which the waste matter is trickled over a large surface consisting of a bed of rock or other porous material on which microbiological growth is allowed to develop. It is possible, in this way, to lower substantially the oxygen demand of the waste water, although so far the method is not practical on volumes encountered from even a small pulp or paper mill. Mill waters containing a very high content of dissolved matter, such as strawboard mill wastes (B.O.D. 600–900 p.p.m.) cannot be satisfactorily treated by trickling filters. For best results with trickling filters, suitable nutrients (phosphates, ammonia, nitrates, etc.) should be added to the liquor to serve as additional food for the microorganisms.

Anaerobic digestion at 33 to 37° C. has shown promise on an experimental scale as a method for treating strong waste such as strawboard mill waste.⁷⁸ In pilot plant operation, it has been shown that strawboard waste from the rotary, beaters, and washers (B.O.D. 3,560), which has been first settled, can be reduced in B.O.D. after digestion at 33° C. by 0.0475 lb. per cubic foot of tank per day with the effluent having a B.O.D. of about 135 p.p.m.⁷⁹ Heat hydrolysis at 350 to 450° F. shows promise of reducing the pollutional value (B.O.D.) of sulfite waste liquor by 60 to 90% at relatively low cost.⁸⁰ Use of sulfite waste liquor for yeast and mold production has not proved to be an economical means of reducing the B.O.D.

⁷⁷ Annual Report, National Council for Stream Improvement, *Paper Trade J.* 130, No. 1: 22–28, 40 (Mar. 16, 1950)

⁷⁸ D. E. Bloodgood and J. C. Hargleroad, *Paper Trade J.* 127, No. 22: 496–501 (Nov. 25, 1948)

⁷⁹ D. E. Bloodgood, *Tappi* 33, No. 7: 317–320 (July, 1950)

⁸⁰ Annual Report, National Council for Stream Improvement, *Paper Trade J.* 130, No. 10: 16–20; No. 11: 22–28, 40 (Mar. 9, Mar. 16, 1950)

WATER

Water is one of the most important raw materials for papermaking. It is used throughout the papermaking process to suspend or carry the fibers and to dissolve added materials. It is used as boiler feed water, for air conditioning, for cooling, for washing pulps, and for drinking purposes. Its properties should not be taken lightly by the paper chemist, because water is one of the most complicated liquids in existence. Water molecules exist in a highly associated state, and this accounts for the abnormally high surface tension, heat of vaporization, specific heat, etc., compared with most other liquids.

Commercial water is never pure and is often of poor quality in the raw state. Most paper mills require high-quality water, because the quality of the finished paper is determined by the quality of the process water. The quality of the water is particularly important in pulp washing, bleaching, sizing, and coloring of paper. In order to obtain satisfactory water, it is often necessary to resort to water treatment. Nearly perfect water is required for high-pressure boilers (900–2,000 p.s.i.).

The impurities in water may be either physical, chemical, or microbiological. Some of the most common impurities are suspended matter, dissolved color, dissolved organic matter, dissolved mineral matter, and microorganisms. Water also contains dissolved gases, e.g., oxygen, carbon dioxide, nitrogen, and hydrogen sulfide. Water dissolves considerable oxygen, the proportion of oxygen to nitrogen being greater in water (33%) than it is in air (21%). This dissolved oxygen may, under some conditions, oxidize cellulose to oxycellulose, react with reducing agents in the pulp, or cause corrosion of the mill equipment.

The source from which the water is obtained determines its properties. In general, water may be classified as either surface water or ground water. Ground water is that obtained from deep wells or springs, whereas surface water is that obtained from streams, rivers, lakes, etc. As a rule, ground waters are colder, contain less organic and other suspended matter, and contain fewer microorganisms than surface waters, but they usually contain more dissolved mineral matter, such as iron and other salts. Surface waters are used by most paper mills, but ground waters are gaining in usage in many parts of the country because they supply a year-round source of

cool, clean water. Surface waters have a mean monthly temperature close to that of the mean monthly air temperature, which means that there is considerable change in the temperature of surface water throughout the year. Surface waters may vary from a temperature of 32° F. to a temperature of 90° F. at different times of the year. In addition, the water temperature on any given day may show quite a variation from the mean monthly air temperature. In comparison, ground waters remain relatively constant in temperature throughout the year. For example, with wells more than 60 ft. in depth, there is practically no variation at all, and for wells in the neighborhood of 30 ft. below the ground, only a variation of 1° F. would be expected.¹ Ground water obtained from depths below 60 ft. begins to show the effects of heating from the earth's temperature, resulting in a 1° F. temperature rise for each 60 to 100 ft. of depth below the zone of surface influence.²

Properties of Water

Among the most important properties of water for papermaking are the following: amount of suspended matter or turbidity, amount of color, presence of taste or odor, amount of dissolved inorganic matter, hardness, alkalinity and pH, and temperature. All these properties are not necessarily important for every purpose to which the water is put; for example, odor is of minor importance in boiler feed water, whereas it is of major importance in the calender water used on paperboard for packaging foodstuffs.

TABLE I
STANDARDS FOR PROCESS WATER

Substance	Maximum permissible limits in p.p.m.			
	Fine papers	Groundwood papers	Kraft papers	
			Bleached	Unbleached
Turbidity as SiO ₂	10	50	40	100
Color in platinum units	5	30	25	100
Total hardness as CaCO ₃	100	200	100	200
Calcium hardness as CaCO ₃	50
Alkalinity to methyl orange as CaCO ₃	75	150	75	150
Iron as Fe	0.1	0.3	0.2	1.0
Manganese as Mn	0.05	0.1	0.1	0.5
Residual chlorine as Cl ₂	2.0
Silica (soluble) as SiO ₂	20	50	50	100
Total dissolved solids	200	500	300	500
Free carbon dioxide as CO ₂	10	10	10	10
Chlorides as chlorine	75

¹ J. B. Graham, *Paper Trade J.* 123, No. 5: 51-57 (Aug. 1, 1946)

² J. B. Graham, *Paper Trade J.* 123, No. 5: 51-57 (Aug. 1, 1946)

Specifications^{3, 4} for water suitable for the manufacture of fine papers (bonds, ledgers, book, and writings), for kraft papers, and for groundwood papers are given in Table I. Certain grades of paper, such as cigarette paper, facial tissue, condenser paper, filter paper, and photosensitive paper may require water of greater purity than that listed for fine papers.

The methods used in water analysis are not described, since water analysis is a specialized subject and cannot be fully treated in this book. For further information, the reader is referred to standard texts on water analysis.⁵ In water analysis, all results should be expressed in parts per million (p.p.m.), rather than in grains per gallon (g.p.g.). However, if grains per gallon are used, they can be converted to parts per million by dividing by 0.0583. If it is desirable to express the results in equivalents per million (e.p.m.), the parts per million can be divided by the equivalent weight of the elements or radical.

Temperature of Water

The temperature of the mill water is of great importance in determining the rate of defibering and beating of the stock. Water temperature affects the sizing operation and also determines the freeness of the stock on the paper machine.

For many purposes, hot or warm water is required about the mill, and in these cases it is an obvious advantage to have a supply of warm, fresh water. Variations in water temperature are undesirable, particularly when the water is used for cooling purposes.

Suspended Matter and Turbidity

Raw water often contains suspended matter. If the suspended particles are finely divided, that is, a matter of a few microns in diameter, this is referred to as turbidity. Turbid water is "dirty" water.

Turbidity measurements are based upon the depth of water required to obliterate the image of a standard candle flame viewed through the water. Standard suspensions of bentonite in distilled water may be used for comparison. The total suspended matter in water can be determined by filtering through an ashless filter paper and weighing the suspended matter collected on the filter paper.

Turbidity may be due to suspended particles of clay, sand, fibers, microorganisms, organic matter, etc. Rivers which flow through cultivated and developed areas are generally high in turbidity. Turbidity as low as 0.5 p.p.m. is plainly visible if the water is held against a light source. For best

³ See TAPPI Standards

⁴ L. B. Miller, *Tech. Paper No. 101*, 5th Annual Water Conference Proceedings, Engineers' Society of Western Pennsylvania

⁵ TAPPI Monograph on Industrial Water, Series No. 1. Tech. Assoc. Pulp and Paper Industry, New York, N. Y. (1942)

results, the turbidity should be below 10 p.p.m. in process water for fine papers, and not more than 50 to 100 p.p.m. for low-grade papers.

Suspended matter is undesirable in process water, because it lowers the color and brightness of the paper. It also increases the ash content, lowers the strength, and increases the dirt content of the paper. The use of muddy water may decrease the strength of paper by as much as 50%. Coarse suspended matter may form holes in the paper during manufacture, and will unduly abrade parts of the paper machine, such as rolls and Fourdrinier wire. It also tends to plug showers and sprays. Suspended matter may be responsible for foaming and boiler scale.

Silica sometimes exists as turbid material in the form of colloiddally dispersed, very slightly ionized, complex silicic acid molecules which, if not removed, become adsorbed by the cellulose and increase the ash content of the paper.⁶ Silica also tends to form scale in high-pressure boilers, and consequently should be kept below 3 to 4 p.p.m. in boiler feed water.

Color

Color is dispersed matter which gives water an off shade. Color may be caused by matter in true solution or by matter which is colloiddally dispersed. Organic color is usually colloiddally dispersed with the particles carrying a negative electric charge.⁷ An example of soluble material which causes color are the iron salts.

Pure water is colorless, but some waters, particularly swamp waters, are badly colored. This color is generally caused by organic matter, such as the gallates and humates, which are derived from decayed organic matter. Iron salts are troublesome with some waters.

Both organic color and iron compounds are strongly adsorbed by pulp fibers. Furthermore, these compounds tend to be coagulated by alum and deposited on the pulp. In either case, there is a marked reduction in brightness of the pulp and, in extreme cases, the bleaching operation may be affected. Dissolved organic matter may also cause trouble in water treatment by interfering with the coagulation of suspended matter.

Color is generally measured by comparing the water with standard color solutions containing a solution of potassium chloroplatinate, platinum, cobaltous chloride, cobalt, and concentrated hydrochloric acid. Standard Nessler tubes are prepared having colors ranging from 5 to 70. The color of the water can be estimated by matching with the nearest sample while viewing vertically downward through the tubes upon a white surface. The results are reported in terms of platinum-cobalt color (the unit being 0.001 g. of platinum per liter).

⁶ L. B. Miller, *Paper Trade J.* 120, No. 9: 84-88 (Mar. 1, 1945)

⁷ A. S. Behrman, R. H. Kean and H. Gustafson, *Paper Trade J.* 92, No. 8: 121-123 (Feb. 19, 1931)

Taste and Odor

Raw water sometimes carries a certain amount of taste and odor. The presence of odor and taste usually is not objectionable in paper mill supply water, but it is definitely objectionable in mills making paperboard for food containers.

Taste and odor are due to the presence of foreign matter in the water, such as certain salts, gases such as hydrogen sulfide, trade wastes from other mills upstream, and decomposition products resulting from decayed matter. Odors sometimes originate in the water-treatment plant, particularly if the sludges and deposits formed in the sedimentation basins are not removed regularly. Treating the water with chlorine often leaves a disagreeable taste, some of which comes from the chlorine itself, but most of which is due to the reaction of chlorine with organic matter in the water. Chloramines do not leave as bad a taste as chlorine, but the chlorophenols are particularly disagreeable from a taste standpoint. Chlorination followed by treatment with chlorine dioxide has been found, in one case, to remove all taste and odor.⁸ Filtration through activated carbon is sometimes used for removing odor.

Oil Content

The oil content of water is important for boiler feed water, since it is considered dangerous to use water containing over 9 p.p.m. of oil in high-pressure boilers. High oil content is also undesirable in waters for making up coating mixtures, surface size, etc., since excess oil in the water may result in spotting of the paper.

The amount of oil in water can be determined by shaking the water with carbon tetrachloride in a large separatory funnel and evaporating the solvent to determine the amount of oil.

Dissolved Inorganic Matter

Natural waters always contain dissolved inorganic matter in the form of salts, bases, or acids. Some of these salts cause trouble in paper manufacture, but others are harmless if not present in too large quantities.

At dilutions prevailing in process water, most of the dissolved inorganic matter exists in a state of complete ionization. Sodium, potassium, calcium, magnesium, chloride, sulfate, bicarbonate, and hydroxyl are among the ions which are usually present. Bicarbonate and hydroxyl ions cause trouble by reacting with alum to form alumina floc which reduces the strength of the paper. Certain combinations of ions are more harmful than others; for example, calcium combined with sulfate ion is not nearly so harmful as calcium combined with bicarbonate. Certain types of dissolved

⁸ A. G. Davenport, Dept. of Scientific and Industrial Research, *Water Pollution Research* 20, No. 1: Abstr. No. 10, (Jan., 1947); 20, No. 3: Abstr. No. 310 (Mar., 1947)

inorganic matter causes hardness in water. This is discussed in the next section.

Iron and manganese compounds are particularly harmful in water because they become adsorbed on pulp fibers, causing discoloration and a change in the bleaching and dyeing properties of the pulp. Furthermore, iron salts promote the growth of *Crenothrix* bacteria, and manganese has been said to promote the growth of algae.⁹ Iron, manganese, and copper have a catalytic effect on the decomposition of bleach, and thus have an adverse effect on the bleaching operation. Manganese is particularly objectionable in bleaching, because the bleach tends to oxidize the manganese to permanganate, which then imparts a reddish color to the fibers. Iron and manganese are very objectionable in water for photographic and blueprint papers. Concentrations of iron in excess of 0.1 to 0.2 p.p.m. cannot be tolerated in water for most fine papers.¹⁰ Manganese should not be present in amounts over 0.05 p.p.m. for high-grade papers.

Iron in water is quite prevalent. However, most surface waters contain less than 0.1 p.p.m. of iron, although ground waters may contain many times this amount. Fortunately, manganese is not so prevalent as iron, although it is found in appreciable quantities in the Middle West and Great Plains.¹¹ In ground waters, iron is usually present as soluble ferrous bicarbonate, but this is readily oxidized to the insoluble oxide by aeration. Less common forms in which iron is found in ground water are as ferrous carbonate, ferrous or ferric sulfate, and iron organic compounds. In surface water, iron is generally present as colloiddally dispersed hydrated ferric hydroxide. Iron and manganese can be removed from water by coagulation at high pH, followed by filtration of the water. Aeration is also helpful. Chlorination, under the proper conditions, aids in the removal of manganese.¹²

Pulp fibers tend to pick up iron from the water. The iron may be held as adsorbed iron or as insoluble iron compounds which are trapped in the fibers. According to Oman,¹³ pulp fibers adsorb iron in the ferric state, but tend to adsorb little or no iron in the ferrous state. Casciani and Storin¹⁴ report that the amount of iron adsorbed by fibers depends upon the acidity and concentration of iron in the water, with water of low pH actually tending to reduce the original iron content of the fibers. Bleaching tends to lower the iron content of the pulp, provided that the wash water is not high

⁹ K. A. Gussena, Dept. of Scientific and Industrial Research, *Water Pollution Research* 20, No. 2: Abstr. No. 178 (Feb., 1947)

¹⁰ L. B. Miller, *Paper Trade J.* 120, No. 9: 84-88 (Mar. 1, 1945)

¹¹ E. R. Mathews, *J. Am. Water Works Assoc.* 39, No. 7: 680-684 (July, 1947)

¹² H. E. Baldwin, TAPPI Survey of Water Technology, *Tappi* 32, No. 2: 86-90 (Feb., 1949)

¹³ H. Oman, *Papir-J.* 15: 91, 107, 116 (1927)

¹⁴ F. Casciani and G. K. Storin, *Paper Trade J.* 115, No. 14: 163-171 (Oct. 1, 1942)

in iron. Casciani and Storin¹⁵ believe, however, that some fibers hold iron by adsorptive forces which resist repeated washing with iron-free water.

Hardness

Hardness is a term used in reference to water containing dissolved salts which have soap-destroying power. Calcium and magnesium are the most common salts in this group, but iron, aluminum, and manganese are also responsible for hardness. Free acid destroys soap, but water containing acid is not considered hard water. Hardness is usually expressed as parts of calcium carbonate per million parts of water.

Hardness is classified as carbonate hardness and non-carbonate hardness. Carbonate hardness is due to the bicarbonate ion, and non-carbonate hardness is caused by ions such as sulfate, chloride, and nitrate. Carbonate hardness is referred to as temporary hardness, because the carbonate is soluble only because of the presence of carbon dioxide and consequently is precipitated when the water is boiled. Non-carbonate hardness is referred to as permanent hardness because it is not removed on boiling of the water. Of the two, temporary hardness is more objectionable.

The most accurate method of measuring total hardness is by calculation from the chemical analysis of the water. Total hardness can be measured also by titrating a sample of the water with a standard solution of pure soap dissolved in alcohol-water until a strong, permanent lather is obtained. Permanent hardness can be determined by boiling a known quantity of water for thirty minutes, making up to the original volume, using boiled, distilled water, filtering, and then determining the hardness remaining in filtrate.

The hardness of water depends upon the locality where the water is obtained, and whether the water is ground water or surface water. Surface waters draining from limestone areas and ground waters obtained from limestone formations have a high total hardness. Graham¹⁶ gives the weighted average hardness of untreated ground waters in the United States at 191 p.p.m., and the weighted average hardness of surface waters as 85 p.p.m. Waters of this hardness are unsatisfactory for most papermaking processes.

Hardness is objectionable for a number of reasons. Hard waters cause sizing difficulties by reacting with rosin size, precipitating part of the size as insoluble calcium or magnesium soaps. Hard waters are not suitable for washing alkaline-cooked pulps, since they react with soluble resinates in the black liquor, thereby forming insoluble soaps which cause trouble in bleaching of the pulp. In the same manner, hardness also leads to pitch trouble. Hard waters sometimes interfere with the dyeing of the paper. Another

¹⁵ F. Casciani and G. K. Storin, *Paper Trade J.* 115, No. 14: 163-171 (Oct. 1, 1942)

¹⁶ J. B. Graham, *Paper Trade J.* 123, No. 5: 51-57 (Aug. 1, 1946)

disadvantage is that certain hard waters release carbon dioxide when the pH of the water is lowered with alum, thereby causing pinholes in the paper or foaming on the machine. Hard waters are most undesirable for boilers and heat exchangers, since they produce scale which interferes with proper heat exchange. Waters containing temporary (bicarbonate) hardness sometimes form scale on paper machine parts where evaporation is excessive, e.g., screens, pumps, etc. Scale is also likely to form where hard water reacts with alum, size, or bleach residues.

The old-time papermaker overcame the trouble which hard water causes in sizing by adding a small amount of alum to the stock in the beater before the rosin size was added. In this way calcium and magnesium bicarbonates were converted into insoluble sulfates which cause less trouble when the rosin size is added. This remedy has the disadvantage of increasing the ash content, which is undesirable for certain grades of paper. It is also an expensive method of destroying alkalinity. Today, more effective and more elaborate processes are available for reducing the hardness of mill waters. The processes used for softening water will be described later in this chapter.

Alkalinity and pH

The total alkalinity and the pH are important properties of water for papermaking. Alkalinity may be caused by carbonates and hydroxides, although it is more often due to carbonates and bicarbonates, and hence is related to hardness. The permissible alkalinity in water for high pressure steam generators is about 50 p.p.m. or less.

The pH of water varies, depending upon its source and the type of process used for treating the water. Most natural surface waters are slightly alkaline, but swamp waters may be somewhat acid. Well waters are frequently acidic in character, because of the presence of free CO₂.

The pH and alkalinity are important because of their effect on the corrosion of equipment, on the sizing and coloring operations, on the flocculation processes, and other similar processes.

Water Treatment

Water treatment is a necessity for mills making high-grade papers. Water treatment may be carried out (1) to improve the quality of the fresh water supply, (2) to recover valuable stock from the white water, or (3) to prevent stream pollution.

In former times, one of the primary considerations in determining the location of a paper mill was the quality of the local water. Today this is not quite so important because of the various processes which are available for treating water. Nevertheless, it is still a marked advantage for a mill

to have access to a plentiful supply of high-grade raw water. The amount of treatment which is necessary depends upon the purity required (i.e., grade of paper being made) and also upon the condition of the raw water.

The various processes used in the treatment of raw water include settling, aeration, chemical treatment to induce flocculation, filtering, disinfection, chemical treatment to remove hardness, etc. All these processes may not be necessary if the raw water is of high quality or if the requirements are not too stringent.

Treatment of raw mill water has long been recognized as a necessary or desirable step, but the treatment of paper mill effluents has only become necessary within recent years. It is now necessary, from an economic standpoint, for all paper mills to recover as much water, fiber, and filler as possible from the mill waste in order to return it to the paper mill system. Furthermore, the pollution of streams has received increasing attention to prevent contamination of domestic water supplies and damage to fishing and other recreational facilities. There is a tendency for state and federal governments to enact stringent legislation governing the disposal of industrial wastes. With greater controls in the offing, it is desirable for paper mills to reduce the biochemical oxygen demand of the water going to the sewer. This chapter is concerned with the treatment of raw mill water. The subject of white water recovery is discussed in Chapter VIII and the subject of mill waste water in Chapter XIV.

Aeration

One of the processes used in water treatment is aeration. Water may be aerated by spraying or bubbling so that air can get to it, or by permitting it to trickle over trays where the water is dispersed into thin films.

Aeration is desirable because: (1) it allows such gases as hydrogen sulfide and carbon dioxide to escape from the water; (2) it increases the absorption of oxygen, thereby oxidizing soluble ferrous iron to the insoluble ferric state; (3) it oxidizes and destroys certain microorganisms which are capable of growth only in the absence of dissolved oxygen; (4) it improves the odor and taste of the water.

On the other hand, too much aeration can be undesirable because: (1) it may increase the oxygen content to the point where the water becomes extremely corrosive; (2) it may tend to oxidize and destroy certain types of toxicants which have been added to the water to prevent microbiological growth.

Sedimentation

In water treatment, one or more sedimentation steps may be involved. If the water contains only a small amount of suspended material which is of the type easily settled out, a single sedimentation may be all the treatment

which is required. However, in most cases, the water must be chemically treated beforehand to increase the amount of sedimentation. This process is called flocculation and is described in the following section. After the water has been treated with the flocculating agent, it is allowed to stand quietly for thirty minutes to four hours in order to settle out the floc which is formed.

Flocculation

Much of the suspended matter in raw water is colloiddally dispersed and cannot be readily removed by sedimentation or filtration. To overcome this difficulty, the water is first treated with flocculating agents. This treatment flocculates the finely divided material into larger agglomerates, which can be removed readily by sedimentation or filtration. This process is known as flocculation, and it constitutes one of the most important processes in water treatment.

The treatment of water with flocculating agents is a classical study in colloid chemistry. The amount and type of coagulating agent required depend on the amount of turbidity and colloiddally dispersed material in the water. The amount required can be fairly accurately determined by treating a small sample of the water with coagulant in the laboratory.

In addition to removing the organic coloring matter and matter causing turbidity, flocculation also helps to remove any taste-bearing substances which may be present. Flocculation helps to remove iron if it is present in the organic or colloiddal form. However, if the iron is present as soluble ferrous carbonate, the water must first be aerated to oxidize and insolubilize the iron. Some bacteria are removed by flocculation, but the spores are not.

In practice, the coagulating chemical is added to the raw water in specially designed tanks and rapidly mixed. The water is then slowly mixed for fifteen to sixty minutes or more to develop the floc and to increase the size of the floc particles. The object of slow mixing is to provide an opportunity for the small flocs to become adsorbed on the larger flocs. A recent development in water treatment has been the use of previously formed sludge to increase the amount of adsorption.¹⁷ In this process, the water is first treated with coagulant and then brought into intimate contact with some of the previously formed sludge and allowed to remain in contact until the new floc is deposited upon the larger particles of the old sludge.

Because flocculation is not an instantaneous process, time must be allowed for the initial molecular precipitates to grow, first into particles of colloiddal dimensions, and eventually into large flocs visible to the naked eye. High temperature increases the rate of growth of the colloiddal particles through its effect on Brownian movement, and also increases the settling rate of the floc because of the reduced viscosity of the water. The flocs

¹⁷ A. F. McConnell, *Paper Trade J.* 112, No. 26: 325-329 (June 26, 1941)

which are formed are settled out in settling basins or filtered out on special filters.

The flocs produced have a tremendous surface, and consequently adsorb and occlude any matter suspended in the raw water, including the coarsely suspended, as well as the colloiddally dispersed matter. The coarsely suspended material becomes entrained in the large flocs, but in the case of the colloiddally dispersed material, something more than physical entrainment is involved. For example, when alum is used as the coagulant, the tri-valent aluminum ions neutralize and coagulate the negatively charged colloidal particles, in accordance with the Hardy-Schultz rule for the coagulation of colloids. This increases the flocculating tendency of the colloidal particles. In such cases, the pH must be controlled to insure the presence of the required amount of aluminum ion, which ordinarily means a pH of 5.0 or lower. This type of coagulation is important in the flocculation of colored swamp waters, waters containing dyestuffs, or waters containing other colloiddally dispersed, negatively charged material.

The chemicals used in flocculation are those which form gelatinous flocs. Alum is the most common flocculating agent, but others which are used include sodium silicate, sodium aluminate, ferric sulfate, ferrous sulfate (copperas), and bentonite. Special starches and animal glues are also used in flocculation. Noreus¹⁸ has described the use of activated silica, which is prepared by treating sodium silicate with ammonium sulfate, ageing until the micelles have grown to the desired size, and then diluting to stabilize the solution. Klinger¹⁹ used activated silica for water treatment and found that it reduces the amount of dissolved silica, as well as the color and turbidity of the water.

Each flocculating agent has its own optimum conditions for floc formation; for example, alum forms a floc best at a pH around 5.5, but redissolves at a high pH , whereas ferric sulfate is effective over the entire pH range above 3.5.²⁰ The use of silica is said to broaden the effective pH range of coagulation with alum so that a satisfactory floc can be obtained at a pH as high as 7.0.²¹

In order to obtain satisfactory results with alum, there must be a minimum quantity of aluminum ion, and the pH must be carefully adjusted. According to Miller,²³ precipitation is most nearly complete when 2.5 equivalents of hydroxyl ion are added per ion of aluminum and this occurs at

¹⁸ R. E. Noreus, *Paper Trade J.* 120, No. 11: 101-103 (Mar. 15, 1945)

¹⁹ L. L. Klinger, *Paper Trade J.* 122, No. 15: 158-164 (Apr. 11, 1946)

²⁰ "Ferrisul," Monsanto Chemical Company, Merrimac Division, Boston, Massachusetts

²¹ L. L. Klinger, *Paper Trade J.* 122, No. 15: 158-164 (Apr. 11, 1946)

²² T. E. Larson and A. M. Buswell, *Ind. Eng. Chem.* 32, No. 1: 130-132 (Jan., 1940)

²³ L. B. Miller, *Paper Trade J.* 108, No. 2: 18-24 (Jan. 12, 1939)

pH around 5.4 to 5.5. The floc generally has its maximum positive electrostatic charge at about this point. The charge becomes less as the pH is increased and reverses to a negative charge at a pH somewhere between 6.2 to 8.2, after which the floc becomes increasingly negative, on account of the adsorption of OH ions. In comparison, magnesium hydroxide is positively charged up to a pH of 12, and calcium carbonate has a negative charge at all pH values.²² The optimum pH varies depending upon the water; for highly colored waters of swampy origin, the optimum pH may be as low as pH 4.0, whereas in the case of very hard waters, it may be as high as pH 8.0.²³ The effect of alkali on the pH of alum solutions is shown in Figure XV-1.²⁴

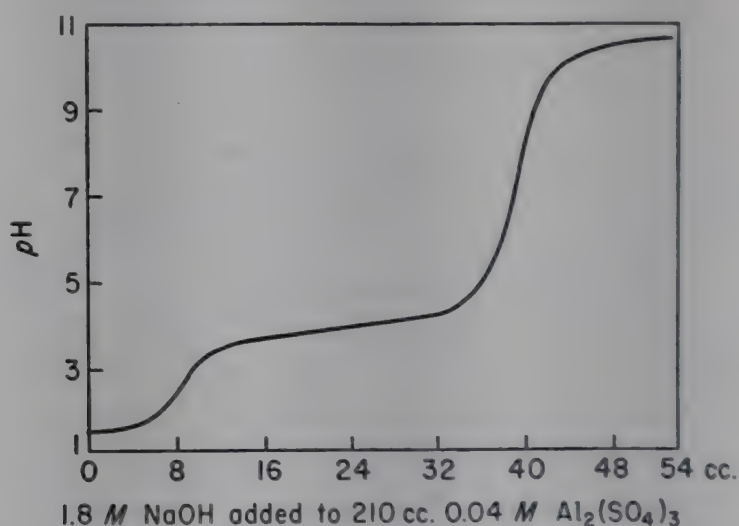


Fig. XV-1. Effect of alkali on the pH of alum solution.

In many cases there is enough alkalinity in the raw water to form a floc when the alum is added, but it is always best to test the water in order to determine the optimum concentrations of alkali and alum for best floc formation. If the water is lacking in alkalinity, or if the turbidity is unusually high, an alkali such as sodium carbonate should be added to increase the amount of floc. Noreus²⁵ found 5 to 9 grains of alum per gallon of water to be the minimum amount required for the coagulation of water containing organic matter. Adams²⁶ lists the following quantities of alum necessary for flocculating turbid waters in the southern regions of the United States:

Turbidity	Dosage of alum
Less than 200 p.p.m.	1 grain per gallon
Around 200 p.p.m.	2 grains per gallon
1,000 p.p.m.	Slightly less than 3 grains per gallon

²⁴ W. O. Milligan, W. R. Purcell and H. B. Weiser, *Ind. Eng. Chem.* 33, No. 5: 669-772 (May, 1941)

²⁵ R. E. Noreus, *Paper Trade J.* 120, No. 11: 101-103 (Mar. 15, 1945)

²⁶ R. R. Adams, *Paper Trade J.* 125, No. 24: 287-291 (Dec. 11, 1947)

To obtain good floc formation with alum, an anion of strong coagulating power must be present. Anions reduce the time for floc formation and extend the zone of coagulation on the acid side. Usually the sulfate ion derived from alum is sufficient.

Bentonite is sometimes used in combination with alum for the treatment of water.²⁷ The bentonite is mixed with the water in a highly dispersed condition and then is coagulated by the calcium and magnesium ions present in the water, or by the alum which is added.²⁸ This forms an extremely voluminous floc which is highly effective in removing coarsely suspended material from the water. Silt particles of extreme fineness are best removed by alum treatment alone.

There are certain substances in raw water which act as protective colloids and inhibit floc formation. For example, leaf tannins are said to impede flocculation, and Griffin²⁹ found that organic iron sometimes interferes with flocculation. By treating raw water with chlorine, it is possible to convert ferrous iron to ferric iron so completely that a good floc results from the iron itself.

Filtration

Filtration involves the removal of flocculated and suspended material so as to produce a clear and sparkling water. Filtration usually follows a preliminary flocculation and sedimentation which removes the coarsely suspended material.

Sand beds are the most common filtering media. Sand filters will not hold back any material which is colloiddally dispersed, since the function of the sand is to retain the gelatinous floc, which serves as the real filtering medium. Sand beds are usually about 2 ft. in depth and contain sand of graded size. The fine sand is contained in the first few inches of depth. According to Hopkins,³⁰ the size of the finest sand should not be smaller than 0.45 mm. in diameter, and when a new sand bed is put into service, all sand finer than this should be scraped from the top of the bed. The filtration rate varies from 2 to 3 g.p.m. per square foot of filter surface. The efficient operation of a filter bed depends upon maintenance of the correct head, proper flow, proper back-washing of bed, and other engineering features.

Other filtering media may be used in place of sand. Activated carbon may be used when it is necessary to remove all taste, odor, and color from

²⁷ H. L. Olin and E. M. Meyers, *Paper Trade J.* 120, No. 10: 92-95 (Mar. 8, 1945)

²⁸ H. L. Olin and H. F. Freeman, *Paper Trade J.* 113, No. 19: 246-250 (Nov. 6, 1941)

²⁹ A. E. Griffin, *Paper Trade J.* 113, No. 9: 95-97 (Aug. 28, 1941)

³⁰ TAPPI Water Committee. "Industrial Water for Pulp, Paper and Paperboard Manufacture," TAPPI Monograph Series No. 1. New York (1942), 145 pp.

the water. Carbon in this form is effective because it selectively adsorbs the substances responsible for taste, odor, and color. The carbon may be used in the form of a filter bed, or it may be mixed with the water early in the water treatment process. When used as a filter, the water should first be flocculated and filtered through a regular sand filter to remove the coarsely suspended matter. Certain types of clays also adsorb materials which are responsible for taste, odor, and color.

Another type of filter uses a blanket of preformed sludge as the filtering medium. Sludge blanket type of clarification units are operated at overflow rates of 2,700 gal. per square foot per twenty-four hours in water treatment.³¹

Softening

Softening of water involves a chemical treatment of the water to reduce or remove the hardness. Softening should not be confused with flocculation, since softening is concerned with the removal of dissolved salts, whereas flocculation is concerned with the removal of colloiddally dispersed material.

The two principal methods for removing hardness are by precipitation and by ion exchange. Another method of reducing hardness is by sequestering calcium ions with sodium hexametaphosphate or other surface-active phosphates. The sequestering of hardness is a temporary measure, since the effect wears off in a few minutes to a few days, depending upon temperature, pH, etc.

There are a large number of water-softening processes. Those which are discussed in this chapter include the cold lime or lime-soda process, the hot lime-soda process, the hot lime-soda-phosphate process, the ion exchange or zeolite process, the ion exchange or Zeo-Karb process, and the ion exchange acid-adsorbing process. In some cases, a simple treatment is satisfactory, but for other special purposes a complete demineralization of the water may be warranted. Miller³² recommends the use of a base exchange process or a process using soda ash for waters with permanent hardness, and a quick lime or hydrated lime and soda or base exchange process for waters with temporary hardness. The preferred process will depend upon total water hardness, requirements of the mill, and other local conditions.

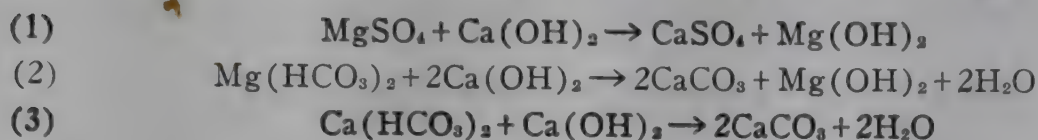
Cold Lime (Lime-Soda) Process of Softening. The cold lime or lime-soda process is a precipitation process. Either straight lime or a mixture of lime and sodium carbonate is added to the cold water and thoroughly mixed.

In this process, the lime changes the bicarbonates in the water into carbonates. The sodium carbonate changes the non-carbonate hardness into carbonates and also precipitates the calcium chloride and calcium sul-

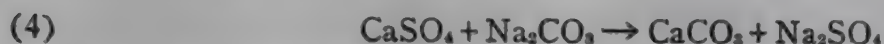
³¹ R. P. Kite and A. J. Fischer, *Ind. Eng. Chem.* 38, No. 1: 16-17, 31 (Jan., 1946)

³² L. B. Miller, *Paper Trade J.* 108, No. 2: 18-24 (Jan. 12, 1939)

fate produced in the lime reactions. The magnesium in the water precipitates as magnesium hydroxide. This results in precipitates which are composed principally of calcium carbonate and magnesium hydroxide. The reactions in lime-soda softening are shown by the following formulas:



Sodium carbonate reacts as follows:



The pH of the water is important and should be adjusted to produce the maximum precipitation of calcium and magnesium. This requires some compromise, since calcium carbonate is least soluble at a pH of 9.4, whereas magnesium hydroxide is least soluble at a pH of 10.8.³³ The precipitates in the process can be removed by settling and filtration. In some cases, the addition of alum is beneficial in producing additional floc which aids in settling of the sludge.

The up-flow type lime and soda softener is a modern development which is being widely accepted for this type of operation and is produced by several different water-treatment equipment manufacturers in varied forms. Modified forms of this equipment are being used for raw water coagulation and clarification and, in modified forms, for the treatment of paper mill white water and other waste products. This type of equipment finds favor because of its smaller size and efficiency, as compared with standard types of coagulation and sedimentation basins. Moreover, the chemical reactions involved (particularly in softening) are carried much more nearly to completion because of the fact that fully reacted sludge is maintained in contact with the water under treatment during the period of chemical reaction.

Hot Lime-Soda Process. The hot lime-soda process is much the same as the cold process, except that the treatment is carried out at temperatures near the boiling point to increase the amount of precipitation. The hot lime-soda process will produce treated water with a hardness lower than 25 p.p.m., or less than 1.5 g.p.g.

One variation of the hot process involves a pretreatment of the water with disodium phosphate ahead of the hot process softener, after which the water is heated and de-aerated to eliminate oxygen and carbon dioxide. After de-aeration, the water is then raised to a pH of about 9.8 with sodium hydroxide in order to precipitate calcium phosphate and magnesium hydroxide. In some cases, this treatment is applied after part of the hardness has been reduced by use of lime and soda ash. Under the best circumstances, it is possible to produce water of almost zero hardness.³⁴

³³ C. E. Imhoff, *Paper Trade J.* 110, No. 14: 195-202 (Apr. 4, 1940)

³⁴ S. D. Distelhorst, *Paper Trade J.* 125, No. 5: 51-54 (July 31, 1947)

Zeolite Process. The zeolite process is an ion exchange process for softening water. It involves passing cold water through a bed of active zeolite, which is a synthetic siliceous compound represented by the general formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_x \cdot (\text{H}_2\text{O})_n$. During this treatment, the hardness is removed by base exchange so that the effluent is zero in hardness.

In the zeolite process, the calcium and magnesium ions in the water are replaced with sodium ions so that the anions such as bicarbonates, sulfates, and hydroxyls, are left in the water in the form of sodium salts. Soluble iron in the form of ferrous salts is also removed by base exchange on zeolite.

In practice, it is necessary to regenerate zeolite periodically with sodium chloride. This replaces the calcium and magnesium ions on the zeolite with sodium ions so that the system will be ready to go through another cycle. One disadvantage, particularly for high-pressure boiler feed water, is the pick-up of silica which results. Another disadvantage is that the solids content of the water is increased.

Zeo-Karb Process. Another type of ion-exchange water softener involves the use of a sulphonated organic material, a carbonaceous zeolite such as Zeo-Karb. This is a cation exchanger containing sulfonic acid groups as the active nuclei.

Zeo-Karb is a cation exchanger like regular zeolite, but it differs from regular zeolite in being able to replace calcium, magnesium, sodium, and other cations with hydrogen. Thus, carbonaceous zeolite goes one step farther than the siliceous type zeolite in that it is able to convert carbonates and bicarbonates into carbonic acid, which can be removed from the water by aeration. Consequently, if the original water contains nothing but carbonates, treatment with Zeo-Karb followed by aeration produces a water equivalent to distilled water.

Carbonaceous zeolite will reduce the iron content of water to 0 to 0.2 p.p.m., since the cations first retained by the zeolite will replace ferrous iron in the water. It is possible to blend water treated with carbonaceous zeolite with water treated with sodium zeolite to obtain water of pH 7. Carbonaceous zeolites are regenerated with acid.

Acid-Adsorbing Process. A new type of water-treating process has been developed recently based upon the use of certain synthetic organic resins which have the ability to adsorb acids from water. When used in conjunction with carbonaceous zeolites, these acid-adsorbing resins produce a completely demineralized water which is equivalent to distilled water, regardless of the type of cations and anions present in the original water.

These acid-adsorbing resins function through active groups, usually amine groups, which act as acid-binding nuclei in a large molecule. Ex-

amples of these materials are aliphatic amine resins and phenylenediamine-formaldehyde resins. The resins in these exchangers can be regenerated with a solution of sodium carbonate and re-used for a number of cycles.

Acid-adsorbing resins are generally used in a two-stage process. In the first stage, the water is passed through a hydrogen cation exchanger (carbonaceous zeolite) to replace all sodium, calcium, magnesium, etc., ions with hydrogen ions. In the second stage, the acid water is passed through the acid adsorber, which results in a water entirely free of ionized compounds. If desired, before passing through the second stage, the water may be aerated to remove any carbon dioxide formed in the first stage as a result of bicarbonates in the raw water.

Although all salts are removed in the above two-stage process, silica tends to pass through the exchanger because it is un-ionized. However, it can be removed by³⁴ (1) adsorption, using magnesium oxide and caustic soda, and (2) treatment of the water with hydrofluoric acid, followed by ion exchange.

Disinfection

The disinfection of water is a very important part of water treatment. It is discussed in the preceding chapter on microbiology.

In most cases, it is desirable to sterilize the water before it enters the water-treatment plant in order to prevent spoilage in the sedimentation basins and filters. Spoilage of sludge in the sedimentation basin releases gases which disturb the sludge and also add bad odor and taste to the water.

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